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NUCLEAR MOMENTS OF ANTIMONY ISOTOPES—DISCUSSION OF LANDÉ'S THEORY[1]

BY M. F. CRAWFORD[2] AND S. BATESON[3]

Abstract

Hyperfine structures in the Sb IV spectrum have been investigated. Analysis of the hyperfine patterns shows that the I-values of Sb_{121} and Sb_{123} are $\frac{5}{2}$ and $\frac{7}{2}$ respectively, in agreement with those deduced by Badami from Sb II. The magnetic moments of Sb_{121} and Sb_{123}, calculated from the hyperfine separations in Sb IV, are 4.0 and 3.2 proton magnetons respectively. For antimony the ratio of the $g(I)$ factors is $g(I)_{121}/g(I)_{123} = 1.82 \pm .02$. The application of the Landé $g(I)$ formula to this accurate ratio leads to a value $g_s = 3$ for the magnetic factor of the proton spin, instead of $g_s = 4$ as found by Landé. The value $g_s = 3$ gives slightly better general agreement between the observed and the calculated $g(I)$ factors than is obtained for $g_s = 4$. However, since no specific value of g_s will satisfy the accurate ratio criterion for all the Z_{odd}, M_{odd} isotopes to which the test can be applied, it is concluded that the theory is incomplete.

Introduction

A spark spectrum involving configurations with an unpaired *s* electron is particularly suitable for hyperfine structure analysis. The high effective nuclear charge in the ion and the large nuclear interaction of the penetrating *s* electron are effective in producing wide magnetic hyperfine separations. The writers' experience with a number of spectra of this type (5, 16, 17, 18*, 19) suggested investigating Sb IV (2, 8) to determine the nuclear moments of the antimony isotopes (15). A cursory examination of the antimony spectrum in the region 3800Å to 2500Å with a three-metre concave grating and a multiple prism spectrograph showed that a number of Sb IV lines have wide, complex structures. The patterns, however, were not sufficiently resolved to be interpreted uniquely. Accordingly the investigation was continued using an instrument of higher dispersion and resolving power. The results obtained are presented and interpreted in this paper. During the course of the investigation Badami (3, 4)† published results on hyperfine structures in Sb I and Sb II, and from his data deduced the I-values $\frac{5}{2}$ and $\frac{7}{2}$ for Sb_{121} and Sb_{123} respectively. These values are in agreement with the values determined by the writers from the structures in Sb IV.

[1] *Manuscript received April 9, 1934.*
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[3] *Holder of a fellowship under the National Research Council of Canada.*

* *Also unpublished data.*
† *See also Murakawa (20).*

Experimental

The lines were excited by an electrodeless discharge in antimony vapor (16). Under the proper experimental conditions this type of source emits lines of high excitation with good intensity. Further the line components show no appreciable broadening due to the Doppler or the Stark effect, and are narrow enough to permit accurate measurement of the hyperfine separations.

The final spectrograms were obtained with a new 21 ft. concave grating spectrograph of the Eagle type. An outstanding feature of the instrument is the design of the plate holder. It has a length of 13 ft. and for an angle of incidence equal to 31.5° photographs the spectral region $n\lambda = 12{,}000$Å to $n\lambda = 21{,}000$Å in one exposure. Thus all lines with wave-lengths of 7000Å or less are recorded in at least two orders, provided the proper plates are used. The spectrograph is enclosed in a double walled room. By means of a thermostatic control the temperature of the room can be maintained so that the fluctuations at the grating are less than 0.01° C. The grating, recently procured from Professor Gale of Chicago, has a radius of curvature of 21.03 ft. and a total of 80,000 lines ruled 600 to the millimetre. This grating gives on one side of the normal a strong, well defined spectrum in the $n\lambda$ region quoted above. The maximum intensity is at $n\lambda = 17{,}000$Å and falls off gradually towards larger and smaller $n\lambda$ values. From the data given above the dispersion can be easily calculated for any value of $n\lambda$. For example, at $n\lambda = 20{,}000$ the dispersion in the fifth order is 0.383Å per millimetre.

A number of exposures ranging from one-half to three hours were taken on Wellington Anti-screen and Ilford Special Rapid Panchromatic plates.

Results and Interpretation

The measured structures are tabulated in Table I. The wave-lengths of the lines are given in the first column, their classifications (2, 8) in the second, and the hyperfine separations in the third. For each hyperfine

TABLE I

HYPERFINE STRUCTURE SEPARATIONS

Wave-length	Classification	Hyperfine structure separations in cm^{-1} $\nu \longrightarrow$							
3735Å	$5s6s\ ^3S_1 - 5s6p\ ^3P_2^o$	(10) 0.00 Sb_{121}	(8) 0.496 Sb_{123}	(6) 2.45 Sb_{123}	(8) 2.82 Sb_{121}	(4) 3.97 Sb_{123}	(4) 4.81 Sb_{121}		
3687Å	$5s6s\ ^3S_1 - 5s6p\ ^3P_1^o$	(5) 0.00	(3) 0.75	(4) 1.23	(4) 1.49	(10) 2.21	(3*d*) 3.14	(6) 4.21	(7*b*) 4.90
3426Å	$5s6s\ ^3S_1 - 5s6p\ ^3P_1^o$	(1) 0.00	(6*a*) 1.07	(4) 1.71	(10*ba*) 2.66	(2) 3.25	(9*ba*) 3.82	(1) 4.38	(4) 4.78
3288Å	$5s6s\ ^3S_1 - 5s6p\ ^3P_1^o$	(8) 0.00	(10) 0.63	(2) 1.22	(10) 2.72	(2) 3.55	(2) 4.14	(1) 4.69	(3) 5.60

NOTE:—*d—broad and diffuse; b—broad but well defined; a—slightly asymmetrical.*

pattern the positions of the components are expressed relative to the red component which is assigned the value 0.00. The intensities, given in brackets, were estimated visually relative to the strongest component which is arbitrarily assigned the value 10.

For the interpretation of the hyperfine patterns it is necessary to consider the contribution of each isotope. According to Aston (1) antimony has two isotopes, Sb_{121} and Sb_{123}, with a relative abundance $Sb_{121} : Sb_{123} = 100 : 80$. When this is taken into account the structures in Table I can be readily interpreted.

3735Å ($5s6s\ ^3S_1 - 5s6p\ ^3P^o_0$)

Theoretically the maximum number of hyperfine components for this multiplet transition is three per isotope. As six components have been observed the line must be completely resolved. The triplet structure for each isotope is characteristic of the $^3S_1$ term, since the $^3P^o_0$ is not split. The splitting of $^3S_1$ into three hyperfine levels shows immediately that the I of each isotope is $\geqslant 1$. The isotopic origins assigned in Table I to the six components are the only allotment consistent with Aston's abundance ratio and the interval rule which requires for $I \geqslant 1$ that the ratio of the intervals between the three components of each isotope be rational and $\leqslant 2$. For this allotment the hyperfine intervals of $^3S_1$ of Sb_{121} are normal and equal to 2.82 and 1.99 cm^{-1}, and those of $^3S_1$ of Sb_{123} are also normal and equal to 1.95 and 1.52 cm^{-1}. An application of the interval rule to these separations gives

$$Sb_{121} : \frac{I+1}{I} = \frac{2.82}{1.99} = 1.41$$

$$Sb_{123} : \frac{I+1}{I} = \frac{1.95}{1.52} = 1.28$$

These ratios definitely fix the I-values of Sb_{121} and Sb_{123} as $\frac{5}{2}$ and $\frac{7}{2}$ respectively.

The above interpretation is represented graphically in Fig. 1. The "calculated" pattern was derived by means of the interval rule from the total separations 4.81 and 3.47 cm^{-1} of the $^3S_1$ of Sb_{121} and Sb_{123} respectively, on the assumption that the centres of gravity of the patterns of both isotopes coincide. The coincidence of the observed and the calculated positions of the two central components confirms the interpretation. The observed intensities are consistent with those calculated by Hill's formulas (11).

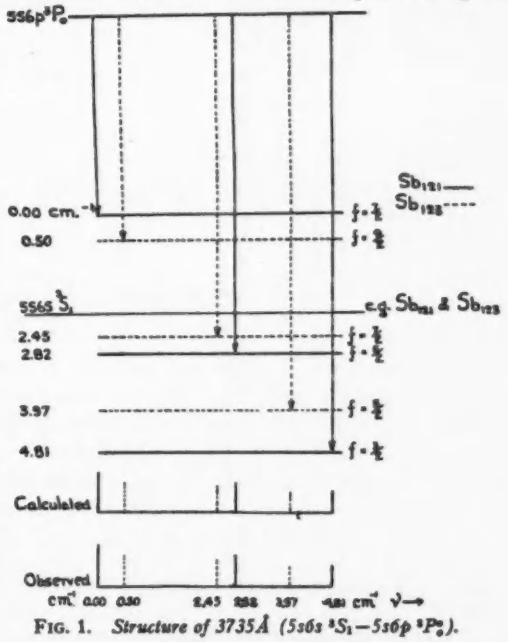

FIG. 1. *Structure of 3735Å ($5s6s\ ^3S_1 - 5s6p\ ^3P^o_0$).*

3687Å ($5s6s\ ^3S_1 - 5s6p\ ^3P_1^o$)

The structure of this transition is only partly resolved. For the I-values $\frac{5}{2}$ (Sb_{121}) and $\frac{7}{2}$ (Sb_{123}) it should have 14 components, 2 of which are expected to be weak (11). Eight components, of which one is diffuse, have been observed. The structure has been interpreted by the graphical method of Fisher and Goudsmit (7). The appropriate graph for a $J=1$ to $J=1$ transition was constructed using the I-value and the total $^3S_1$ hyperfine interval for each isotope obtained from 3735Å. The graphs for the two isotopes were superimposed with their c.g.'s coinciding to form a composite graph. The observed pattern fits this graph well for an interval factor ratio $A(^3P_1^o)/A(^3S_1) = 0.800$. The best fit indicates that the c.g. of Sb_{123} is 0.02 cm^{-1} to the red of c.g. (Sb_{121}), but this shift is not significant as it is of the same order as the uncertainty in the measured separations between components. The complete interpretation is represented graphically in Fig. 2. The positions of the components in the "calculated" pattern are those given by the composite graph for $A(^3P_1^o)/A(^3S_1) = 0.800$. The theoretical intensities (11) of the components are represented by the heights of the lines. The agreement between the calculated and the observed structure is good.

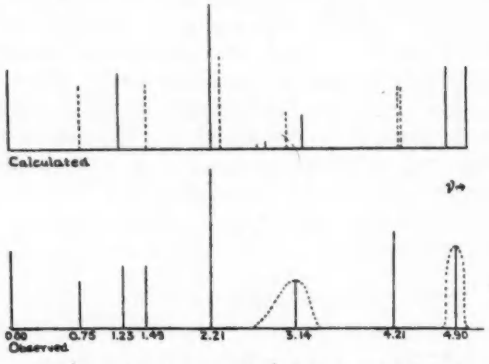

FIG. 2. *Structure of 3687Å ($5s6s\ ^3S_1 - 5s6p\ ^3P_1^o$).*

3425Å ($5s6s\ ^3S_1 - 5s6p\ ^3P_2^o$)

Eight distinct components have been observed for this transition. The pattern was interpreted in a manner similar to that described for 3687Å. A satisfactory interpretation is obtained only when c.g. (Sb_{121}) is made to coincide with c.g. (Sb_{123}). The observed pattern fits the composite graph at $A(^3P_2^o)/A(^3S_1) = 0.420$. The observed and calculated patterns are compared in Fig. 3. The agreement is satisfactory.

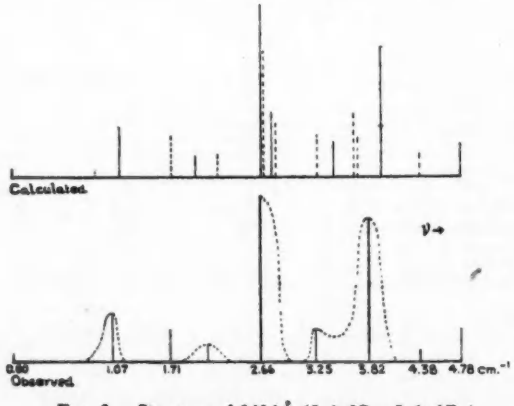

FIG. 3. *Structure of 3426Å ($5s6s\ ^3S_1 - 5s6p\ ^3P_2^o$).*

3288Å ($5s6s\ ^3S_1 - 5s6p\ ^1P_1^o$)

Eight components have been observed for this transition. Although the pattern is comparatively weak, the outermost components appear with moderate intensity; hence the total hyperfine separation can be measured quite accurately. As this splitting is considerably greater than that of the $^3S_1$ (Sb_{121}) alone, the line pattern must be fitted to that portion of the graph corresponding to a negative value of $A(^1P_1^o)$. The graphical analysis shows that the c.g.'s coincide and that $A(^1P_1^o)/A(^3S_1) = -0.281$. The calculated and observed patterns are presented in Fig. 4.

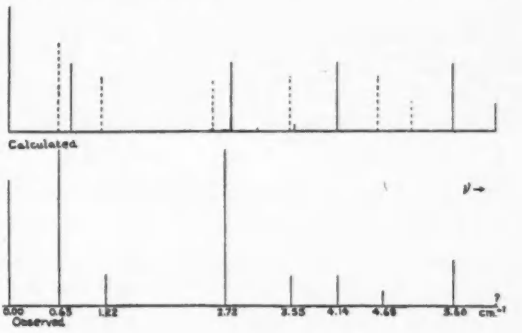

FIG. 4. *Structure of 3288Å ($5s6s\ ^3S_1 - 5s6p\ ^1P_1^o$).*

TABLE II

TOTAL SEPARATIONS AND INTERVAL FACTORS

Term	Total Hfs. separation, cm^{-1}		Interval factor, A. cm^{-1}	
	Sb_{121}	Sb_{123}	Sb_{121}	Sb_{123}
$5s6s\ ^3S_1$	4.80	3.47	0.800	0.434
$5s6p\ ^3P_0^o$	Unsplit	—	—	—
$^3P_1^o$	3.84	2.78	0.640	0.347
$^3P_2^o$	4.03	2.91	0.336	0.182
$^1P_1^o$	−1.35	−0.98	−0.225	−0.122

The data obtained from the preceding analysis are summarized in Table II. No isotope shifts greater than the uncertainty in the writers' measurements ($0.02\ cm^{-1}$) were observed. This means that the c.g.'s of the hyperfine levels of Sb_{121} and Sb_{123} coincide or have the same shift for all five terms in Table II.

Theoretical Discussion

g(I) Factors and Magnetic Moments

In the following the interval factors listed in Table II are compared with theory, and the interaction constants of the valence electrons are evaluated. The calculations are carried out only for Sb_{121}. Since the ratio of the interval factors of the two isotopes is constant (A, Sb_{121})/(A, Sb_{123})=1.84, for all terms, the interaction constants for Sb_{123} can be obtained directly from those for Sb_{121} by dividing the latter by 1.84.

5s6s—The expression for the interval factor of $^3S_1$ is

$$A(^3S_1) = \tfrac{1}{2}(a_{5s} + a_{6s}) = 0.800\ cm^{-1}\ , \qquad (1)$$

where a_{5s} and a_{6s} are the interaction constants of the two valence electrons. Since this is the only equation involving the two constants, they can not be evaluated directly from the interval factor. However, as a_{6s} is much smaller

than a_{5s} its contribution can be estimated with sufficient accuracy as follows. According to theory (21, p. 209, ref. 1; and p. 210) the expressions for a_{5s} and a_{6s} differ only in the factor

$$Z_i.Z_o^4/n_{eff}^3 . \tag{2}$$

Z_i is the same for both electrons. For the 5*s* electron, $Z_o=5$, $n_{eff}=2.47$ as determined from the term value of $5s\ ^2S$ of Sb V. For the 6*s* electron, $Z_o=4$, $n_{eff}=3.50$ obtained by adding about one unit to the n_{eff} of 5*s*. The substitution of these values in Relation (2) gives

$$a_{5s}/a_{6s}=4.45. \tag{3}$$

The values of the interaction constants obtained by substituting this ratio in Equation (1) are a_{5s} $(Sb_{121})=1.31$ cm^{-1}, a_{6s} $(Sb_{121})=0.29$ cm^{-1}.

5s6p—The coupling in this configuration tends towards (*jj*). For (*jj*) coupling the interval factor expressions are (9)

$$\begin{aligned} 5s6p_{\frac{1}{2}},\ J=1 &: A(^3P_1^o)=\tfrac{1}{2}a_{5s}+\tfrac{1}{2}a_{6p}(\tfrac{1}{2}) \\ 5s6p_{1\frac{1}{2}},\ J=2 &: A(^3P_2^o)=\tfrac{1}{2}a_{5s}+\tfrac{1}{2}a_{6p}(1\tfrac{1}{2}) \\ 5s6p_{1\frac{1}{2}},\ J=1 &: A(^1P_1^o)=-\tfrac{1}{2}a_{5s}+\tfrac{1}{2}.a_{6p}(1\tfrac{1}{2}) \end{aligned} \tag{4}$$

where $a_{6p}(\frac{1}{2})$ and $a_{6p}(1\frac{1}{2})$ are the interaction constants of the 6*p* electron with $j=\frac{1}{2}$ and $j=1\frac{1}{2}$ respectively, and a_{5s} is the interaction constant of the 5*s* electron. According to Goudsmit (10), and Fermi and Segrè (6)

$$a_{6p}(j)=\frac{R\alpha^2Z_iZ_o^4}{n_{eff}^3\,l(l+1)\,(l+\frac{1}{2})}\cdot\frac{g(I)}{1838}\cdot\frac{l(l+1)}{j(j+1)}\cdot K(j,Z_i)=a_{6p}\cdot\frac{l(l+1)}{j(j+1)}\cdot K(j,Z_i), \tag{5}$$

where a_{6p} is an abbreviation for the first two terms, $K(j, Z_i)$ is the relativistic correction, and $j=\frac{1}{2}$, $1\frac{1}{2}$ for a *p* electron. For the 6*p* of Sb, $Z_i=(Z-4)$, and the corresponding relativistic corrections are $K(\frac{1}{2}, 47)=1.26$ and $K(1\frac{1}{2}, 47)=1.04$ (10). On substituting the values of $a_{6p}(j)$ obtained from Equation (5) in Equations (4) the latter reduce to

$$\begin{aligned} A(^3P_1^o) &= \tfrac{1}{2}a_{5s}+1.68a_{6p} \\ A(^3P_2^o) &= \tfrac{1}{2}a_{5s}+0.41a_{6p} \\ A(^1P_1^o) &= -\tfrac{1}{2}a_{5s}+0.69a_{6p} \end{aligned} \tag{6}$$

Since the coupling is not strictly (*jj*), it is advisable to apply the above equations in the sum form rather than individually. The sum relations are

$$\begin{aligned} A(^3P_1^o)+A(^1P_1^o) &= \tfrac{1}{2}a_{5s}+2.37a_{6p}=0.415\,\text{cm}^{-1} \\ A(^3P_2^o) &= \tfrac{1}{2}a_{5s}+0.41a_{6p}=0.336\,\text{cm}^{-1}. \end{aligned} \tag{7}$$

Whence $a_{5s}=1.28$ cm^{-1}, and $a_{6p}=0.040$ cm^{-1}. Racah's equations (22) for intermediate coupling are also applicable to the individual interval factors of *5s6p*, since the distribution of the terms is consistent with Houston's equations (12). In this case the interaction constants can be evaluated from any two of the interval factors and can be substituted in the expression for the third to test the consistency of the solution. Racah's equations are found to have a consistent solution and give the same values of a_{5s} and a_{6p} as obtained above. It is to be noted that the values of a_{5s} obtained from *5s6s* and *5s6p* are in good agreement.

The $g(I)$ factor can be evaluated independently from one of a_{5s} a_{6s}, and from a_{6p}. For the s electrons $g(I)$ is given by the formula (10)

$$g(I) = \tfrac{2}{3} \frac{a_{ns} \cdot n^3_{eff} \cdot}{R\alpha^2 Z_i Z_o^2} \frac{1838}{K(\frac{1}{2}, Z_i)}. \tag{8}$$

For $5s$: $Z_i = 51$, $Z_o = 5$, $n_{eff} = 2.47$, $K(\frac{1}{2}, 51) = 1.31$, $a_{5s} = 1.3$ cm^{-1}. These values substituted in Equation (8) give $g(I) = 1.4$ proton magnetons. An independent evaluation of $g(I)$ cannot be obtained from both a_{5s} and a_{6s}. In view of Relation (2) both must give the same value of $g(I)$. For the $6p$ electron the formula for $g(I)$ is (10)

$$g(I) = \frac{a_{6p} \cdot Z_i(l+\frac{1}{2}) \cdot \lambda(l, Z_i)}{\Delta\nu} \quad 1838 \tag{9}$$

For $6p$ of Sb IV: $Z_i = (Z-4) = 47$, $l = 1$, $\lambda(1, 47) = 1.04$, $a_{6p} = 0.040$ cm^{-1}, $\Delta\nu = \Delta^3P^o = 2416$ cm^{-1}. These values substituted in Equation (9) give $g(I) = 2.2$ p.m.

The value of $g(I)$ deduced from a_{5s} is by far the more reliable. The value obtained from a_{6p} is of the same order of magnitude but merits little weight: since, first, the value of a_{6p} is very small; second, the relativistic corrections used in Equations (7) are strictly valid for extreme (jj) coupling only; third, any slight perturbation of $5s6p$ by other configurations would produce a large percentage error in a_{6p}, and finally there is still some uncertainty as to the degree of accuracy of Equation (9).

In the derivation of $g(I)$ from a_{5s} the values of Z_o and n_{eff} of the $5s$ electron of Sb IV were taken equal to those of the $5s$ electron of Sb V. The validity of the calculation then involves the assumption that the interaction constant of the $5s$ electron is not appreciably altered by the presence of the $6s$ electron. In the analogous two-electron spectra, Tl II, Pb III, Bi IV (16, 17, 18†, 19) the interaction constant of the more firmly bound s electron increases slightly as the second electron is removed to ionization. Thus $g(I) = 1.4$ calculated from a_{5s} of the $5s6s$ configuration is a lower limit. In Tl II, Pb III, and Bi IV the a_{6s} calculated from $A(6s7s\ ^3S)$ by neglecting a_{7s} is slightly larger than the a_{6s} obtained from $A(6s\ ^2S)$ of the next stage of ionization; *i.e.*, the contribution of the $7s$ electron to $A(^3S)$ more than compensates for the decrease in $A(^3S)$ produced by the screening effect of $7s$ on $6s$. It appears, therefore, that in antimony an upper limit for $g(I)$ is obtained by neglecting a_{6s} and taking $\frac{1}{2}a_{5s} = A(5s6s\ ^3S_1) = 0.800$. This gives $a_{5s} = 1.6$ cm^{-1}. $g(I)$ computed from this value by Equation (8) is 1.7 p.m. These considerations place the value of $g(I)$ between 1.4 and 1.7 p.m. $g(I) = 1.6$ appears from personal judgment to be a fair estimate.

The writers' analysis leads to a $g(I)$ value appreciably larger than the value 1.1 derived by Goudsmit (10) from Badami's measurements. It is presumed that Goudsmit obtained his value from the data* on the $5p6s$ configuration of Sb II, since an analysis of this data by the writers gives his value. One

† *Also unpublished data.*

* *A number of the Sb II lines examined by Badami appear on the writers' spectrograms. The writers' measurements of the structures of these lines are in good agreement with Badami's.*

expects large mutual perturbation between the $5p6s$ and $5s5p^3$ configurations of Sb II, since they are adjacent and of the same parity. An application of Houston's equations (12) to the $5p6s$ terms confirms this. As the hyperfine structures of the $5s5p^3$ terms are large, the interval factors of the terms of both configurations probably depart appreciably from those predicted assuming no perturbation (6). In view of this there is some uncertainty in the value of $g(I)$ deduced from the hyperfine structures of the $5p6s$ terms of Sb II. The $5s6s$ and $5s6p$ configurations of Sb IV are comparatively free from the above criticism. $5s5d\ ^3D_1$ and $5p^2\ ^3P_1$ appear to be the only terms that might perturb $5s6s\ ^3S_1$. Since these two terms have smaller interval factors than $^3S_1$ and are comparatively remote, their perturbing effect on $A(^3S_1)$, as in the analogous spectra Tl II, Pb III, Bi IV (5, 16, 17, 18*, 19), must be small (6). The $5s6p$ configuration apparently is unperturbed since Houston's equations are well obeyed. $4d^95s^25p$, which has not been identified, appears to be the only configuration likely to perturb; but since it has no unpaired electron its perturbing effect on $5s6p$ would introduce no appreciable error in the value of a_{5s} derived from the $5s6p$ interval factors. The consistency of the values of a_{5s} deduced from $5s6s$ and $5s6p$ further supports this conclusion. In view of the above considerations the value of $g(I)$ obtained from Sb IV must be given more weight than the value obtained from Sb II.

The writers' data on the nuclear moments of antimony are summarized here:
Sb_{121} : $I=\frac{5}{2}$; $g(I)=1.6$; magnetic moment $=I.g(I)=4.0$ p.m.; $\frac{g(I)_{121}}{g(I)_{123}}=1.84$
Sb_{123} : $I=\frac{7}{2}$; $g(I)=0.9$; magnetic moment $=I.g(I)=3.1$ p.m.;

Landé's Theory of Nuclear Moments

Landé (14) has calculated the $g(I)$ factors for the Z odd, M odd nuclei on the assumption that the nuclear mechanical and magnetic moments arise from the spin and orbital motions of a single proton. Combining the spin vector, $s=\frac{1}{2}$, and the orbital vector, l, he obtains the general equation for the nuclear g-factor

$$g(I)=g_l\cdot\frac{l(l+1)+I(I+1)-s(s+1)}{2I(I+1)}+g_s\cdot\frac{s(s+1)+I(I+1)-l(l+1)}{2I(I+1)} \qquad (10)$$

For g_s (magnetic factor of proton spin) $=4$ and g_l (magnetic factor of orbital moment) $=1$, he obtains striking general agreement between the calculated and observed $g(I)$ factors. However as the experimental $g(I)$ values are only approximate, the theory cannot be critically tested, especially in regard to the value of g_s. The data on antimony afford a more critical test. Although the $g(I)$ factors of the antimony isotopes are still subject to the uncertainty inherent in the theoretical calculations, the ratio of the $g(I)$ factors is accurately known to be equal to $1.82\pm2\%$ from both the writers' measurements and Badami's. Substituting the appropriate I and $g_l=1$ in Equation (10), the $g(I)$ of each isotope is obtained as a function of the l of the isotope and g_s. Dividing the expression for $g(I)_{121}$ by that for $g(I)_{123}$, the ratio $g(I)_{121}/g(I)_{123}$ reduces to a function of l_{121}, l_{123} and g_s. When the expression for this ratio is

* *Also unpublished data.*

equated to the experimental value 1.80 and solved, the following equation for g_s is obtained:

$$l_{121}(l_{121}+1) - l_{123}(l_{123}+1) = 7\,\frac{1+g_s}{1-g_s} \tag{11}$$

There are four possible solutions of this equation corresponding to the four l values that satisfy the relations $l_{121}\pm\frac{1}{2}=\frac{5}{2}$ and $l_{123}\pm\frac{1}{2}=\frac{7}{2}$. The solutions are given in Table III.

TABLE III

SOLUTIONS OF EQUATION (11)

l_{123} \ l_{121}	2	3
3	$g_s=-13$	$g_s=-1$
4	$g_s=3$	$g_s=15$

Any one of the four g_s values will satisfy the $g(I)$ ratio criterion for the $g(I)$'s of antimony; but according to Landé's theory only $g_s=3$ is compatible with the sense and magnitude of the magnetic moments of not only antimony but also of the other Z odd, M odd isotopes.

The accurate experimental criterion $g(I)_{121}/g(I)_{123}=1.80$ excludes for antimony Landé's value $g_s=4$, since this value predicts $g(I)_{121}/g(I)_{123}=2.4$. $g_s=3$ does accurately satisfy the g(I) ratio in antimony, and in addition gives for other Z odd, M odd isotopes slightly better general agreement between the calculated and the experimental $g(I)$ values than can be obtained for $g_s=4$. In Table IV the $g(I)$ factors calculated for $g_s=3$ and $g_s=4$ are compared with the experimental values.

TABLE IV

CALCULATED AND EXPERIMENTAL $g(I)$ FACTORS

Nucl. (Z)	I (obs.)	g(I) (obs.) Goudsmit (10)	g(I) (obs.) Fermi (6)	g(I) (obs.) Authors	g(I) (theor.) $g_s=3$	g(I) (theor.) $g_s=4$	l
Li_7 (3)	$1\frac{1}{2}$	2.19	—	—	1.7	2.0	1
Na_{23} (11)	$1\frac{1}{2}$	—	1.3	—	1.7	2.0	1
Al_{27} (13)	$\frac{5}{2}$	4.2	—	—	3.0	4.0	0
Cu_{63} (29)	$1\frac{1}{2}$	1.7	1.6	—	1.7	2.0	1
Cu_{65} (29)	$1\frac{1}{2}$	1.7	1.6	—	1.7	2.0	1
Ga_{69} (31)	$1\frac{1}{2}$	1.3	1.4	—	1.7	2.0	1
Ga_{71} (31)	$1\frac{1}{2}$	1.7	1.8	—	1.7	2.0	1
As_{75} (33)	$1\frac{1}{2}$	—	—	1.1*	1.7	2.0	1
					0.6	0.4	2
Rb_{85} (37)	$2\frac{1}{2}$	0.56	0.54	—	0.71	0.57	3
Rb_{87} (37)	$1\frac{1}{2}$	1.87	1.85 (13)	—	1.7	2.0	1
In_{115} (49)	$4\frac{1}{2}$	1.2	1.2	—	1.2	1.3	4
Sb_{121} (51)	$2\frac{1}{2}$	—	—	1.6	1.4	1.6	2
Sb_{123} (51)	$3\frac{1}{2}$	—	—	0.90	0.78	0.67	4
Cs_{133} (55)	$3\frac{1}{2}$	—	0.75	—	0.78	0.67	4
Tl_{203} (81)	$\frac{1}{2}$	3.6	2.8	—	3.0	4.0	0
Tl_{205} (81)	$\frac{1}{2}$	3.6	2.8	—	3.0	4.0	0
Bi_{209} (83)	$4\frac{1}{2}$	0.89	0.79	—	0.82	0.73	5

* *Calculated from the data by M. F. Crawford and A. M. Crooker (5).*

The experimental $g(I)$ values for Na_{23}, Cu_{63}, Cu_{65}, Ga_{69}, Ga_{71}, As_{75}, In_{115}, Sb_{123}, Cs_{133}, Tl_{203}, Tl_{205}, Bi_{209}, are in better agreement with the $g(I)$ values calculated for $g_s=3$ than with those calculated for $g_s=4$. For Li_7, Al_{27}, Rb_{85}, Sb_{121}, better agreement is obtained for $g_s=4$. Rb_{87} is intermediate. The more accurate criterion of the $g(I)$ ratio can be applied only to Cu, Ga, Rb, Sb, and Tl. In the cases of Cu and Tl, for each of which the isotopes have the same I and $g(I)$ values, it is not possible to differentiate between $g_s=3$ and $g_s=4$, since the ratios are satisfied for any value of g_s. Neither $g_s=3$ nor $g_s=4$ satisfy the experimental $g(I)$ ratio in Ga. From Kopfermann's data (13), the $g(I)$ ratio for Rb is 3.40. This is considerably higher than the value 2.33 obtained for $g_s=3$, but it is in fair agreement with the value 3.50 given by $g_s=4$. As pointed out before, the $g(I)$ ratio in antimony is satisfied by $g_s=3$, but not by $g_s=4$. Thus summarizing: $g_s=4$ satisfies the $g(I)$ ratio in Rb but not in Sb; $g_s=3$ satisfies the ratio in Sb but not in Rb; both fail in the case of Ga; the cases of Cu and Tl are indecisive. The general agreement between the observed and calculated $g(I)$ factors favors $g_s=3$. However, it appears since no specific g_s value satisfies the critical $g(I)$ ratio criterion for all cases, that the theory is incomplete as indicated by Landé.

Acknowledgment

The authors wish to thank Professor E. F. Burton, Director of this laboratory, for his interest in the investigation.

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THE THERMAL DEHYDRATION OR DECOMPOSITION OF CERTAIN MINERALS AND SALTS[1]

By A. F. Gill[2]

Abstract

A description is given of a thermal decomposition apparatus in use for some years in the author's laboratory. This consists of an improved form of the familiar combination of calcining furnace and weighing balance, which allows continuous weight determinations to be made of samples undergoing thermal decomposition. The accuracy of the results is enhanced by the provision of a thermocouple suspended directly in the charge and supported by the balance, the necessary connecting leads being as fine as possible without adding significantly to the resistance of the pyrometer circuit.

Thermal decomposition data are given for a number of minerals and salts which undergo loss of water or other constituents, and concerning which practical data of a reasonable degree of accuracy have from time to time been desired. These include, magnesite, hydromagnesite, magnesitic dolomite, dolomite, serpentine, asbestos, calcium and magnesium hydroxides, gypsum, hydrous magnesium sulphate, hydrous aluminium chloride, pyrite and certain samples of coal of high "volatile" content.

Introduction

There are numerous minerals and chemicals whose utilization depends in large measure upon calcination or roasting operations. Common reactions of this type are the decomposition of carbonates and hydroxides, and the dehydration of compounds containing water of crystallization.

As the temperature involved becomes higher, the difficulty in making accurate measurements of thermal decomposition points becomes correspondingly greater. As a consequence accurate data are lacking in the literature for a great many materials which are in comparatively common use.

Some years ago, information was required in this laboratory on the thermal decomposition of natural calcium and magnesium carbonates, both unassociated and as minerals of the dolomite class. While the decomposition point of calcium carbonate was known to a reasonable degree of accuracy, there was considerable conflict in the literature as to its behavior when associated with magnesium carbonate. Part of this uncertainty was due, no doubt, to the fact that vapor pressure measurements have been largely used in laboratory investigations. This method is not always a very convenient one, especially when the decomposition being investigated takes place in several stages, at relatively high temperatures.

Apparatus and Methods

As the information desired was essentially of a practical nature, work was undertaken with the more convenient apparatus which involves decomposition measurements by the suspension of the sample, in a furnace, from one arm of a balance. Apparatus of this type is well known, and is in daily use in, for example, the paper industry. Its disadvantage lies in the difficulty of

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obtaining accurate temperature measurement, as a thermocouple in the body of the furnace will not indicate accurately the temperature of a decomposing sample separately suspended. It was found, however, that if a sufficiently large apparatus were used, a thermocouple could be embedded in the charge itself without the necessary lead wires affecting unduly the sensitiveness of the balance.

An apparatus constructed in this way gave very satisfactory information on the calcium and magnesium carbonates, and quickly proved its value in the commercial developments arising from the results. Since that time, it has been used on various occasions in the laboratory when different materials have been under investigation. As some of the results are of general interest, there are given below a more precise description of the apparatus and some of the decomposition results obtained.

The balance used had a capacity of three kilograms. It was set up on an insulated table, sufficiently high above an electric muffle furnace to avoid any undue heating. The furnace was a well known multiple-heat design of 5 k.w. capacity. A large quartz crucible carried the charge. It was suspended in a cradle of nickel-chromium wire, from which a single strand extended through the furnace cover. A platinum-rhodium thermocouple was attached to the supporting leads, with its hot junction as near as possible to the centre of the charge. Fine copper leads connected the cold end of the thermocouple with the potentiometer. Cold-end temperatures were measured with a thermometer in close proximity to the wires, but hung independently of the crucible support. Calibration of the pyrometric equipment showed no significant reduction in millivoltage with the length of leads used. The crucible was fitted with a nickel cover (in some cases stainless steel) and the furnace itself was insulated at the top and bottom, in order to give a temperature as uniform as possible. A "pilot" thermocouple of base metal was kept in the body of the furnace. With this apparatus the accuracy of the weighings was well within 0.1 gm. With samples of 200 gm. or more, this gave a maximum error to this factor of less than 0.05%. During rapid decomposition, weighing was more difficult; errors were, however, of little practical significance, owing to the fact that at such times, temperatures tended to remain constant.

In early experiments, it was customary to raise the outer temperature at a uniform rate of about two degrees per minute. For materials of low thermal conductivity it was later found desirable merely to maintain a temperature difference of about 50° C. between the thermocouples.

Moderately coarse particles were found to give better results in the tests, and samples, when possible, were sized to minus 4 and plus 40 mesh. During steady decomposition there was little opportunity for air to enter the crucible containing the sample, although this would tend to happen after active evolution had ceased.

Under ideal conditions, such an apparatus would give a constant temperature for the whole period of decomposition. Actually, however, there is bound to be a rounding of the ends of the otherwise sharp curve, owing to

the fact that at the beginning of the decomposition there is lacking a full atmosphere of gaseous products, and more particularly that the outside of the charge is at a higher temperature than the central portion. While this detracts from the quantitative value of the results, their practical utility is not greatly affected.

Experimental Results

Natural Magnesium and Calcium Carbonates

Fig. 1 shows the decomposition of "Washington" magnesite, "Grenville" magnesitic dolomite and "Portage du Fort" dolomite. It was drawn from the original test data from which was developed a process of selective calcination of the magnesitic dolomite to effect decomposition of the magnesium carbonate in the presence of the calcium carbonate.

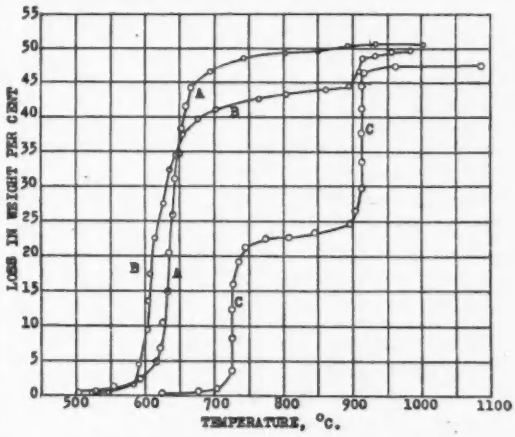

FIG 1. *A, magnesite; B, magnesitic dolomite; C, dolomite.*

Curve *A* shows the most constant value for the decomposition point of magnesium carbonate. The temperature of 640–650° C. may be taken as that of maximum decomposition. This value is of interest chiefly in confirming Curve *B*, which shows this point much less accurately.

This magnesitic dolomite is known, from mineralogical data, to be a mixture of magnesium carbonate and true dolomite ($MgCO_3 . CaCO_3$). Consequently, after the determination recorded in Curve *C* several attempts were made to obtain definite evidence of a similar decomposition point for the magnesium carbonate component of dolomite in this material. The failure to do this, together with the lack of definition of the normal magnesium carbonate decomposition, is ascribed in part to the shortcomings of the method as mentioned above and in part to the presence of some serpentine, the evolution of moisture from which would reduce the partial pressure of the carbon dioxide. It is evident, however, that the decomposition of normal magnesium carbonate is complete at about 650° C.

Curve *C* is of considerable interest in illustrating the behavior of the two carbon dioxide molecules in dolomite. It is seen that the magnesium carbonate component is stable to approximately 725° C., some 75° C. higher than the decomposition point of free magnesium carbonate. The calcium carbonate component, on the other hand, decomposes at the same temperature as free calcium carbonate, approximately 187° higher.

TABLE I

ANALYSES OF INORGANIC SAMPLES

Specimen	Magnesitic dolomite	Magnesite	Dolomite	Serpentine	Asbestos			Gypsum	Magnesium hydroxide	Calcium hydroxide	Magnesium sulphate	Pyrite	Hydromagnesite
					Canadian spinning stock	Arizona crude	Russian crude						
SiO_2	1.4	2.4	0.4	36.4	40.5	41.1	40.7	0.6	—	—	—	4.8	4.6
Al_2O_3	1.3	1.2	0.4	1.5	3.2	4.1	4.6	0.3	—	—	—	(Fe) 46.5	0.7
Fe_2O_3					0.6	0.8	1.3						
FeO	—	—	—	—	1.8	0.2	2.3	—	—	—	—	—	—
CaO	8.4	1.3	30.9	4.3	trace	0.5	trace	32.9	1.7	74.8	—	1.8	1.1
MgO	39.4	44.6	21.5	38.6	39.5	38.8	36.9	0.0	67.2	—	16.3	0.9	40.4
CO_2	49.5	50.5	46.8	5.7	0.2	0.6	0.2	2.6	2.0	2.1	0.2	—	36.5
H_2O comb.	—	—	—	12.0	14.0	14.9	14.3	19.7	29.2	23.2	50.8	—	15.8
H_2O free	—	—	—	1.5	—	—	—	—	—	—	—	—	—
SO_3	—	—	—	—	—	—	—	43.9	—	—	32.4	—	0.15
S	—	—	—	—	—	—	—	—	—	—	—	43.3	—

From the chemical analyses, which are given in Table I, the approximate combinations of carbon dioxide shown in Table II may be deduced, assuming all calcium oxide to exist in carbonates.

TABLE II

EMPIRICAL COMPOSITION OF CARBONATES

—	*A*	*B*	*C*
CO_2 as $CaCO_3$, %	1.0	6.6	24.3
CO_2 as $MgCO_3$, %	49.5	42.9	22.5

It will be noted that *A* and *C* do not give results concordant with the MgO as determined by analysis. More precise calculations are impossible, however, owing to the uncertain condition of the silica and other impurities.

British Columbia Hydromagnesite

Work was done some years ago on this material. The chemical analysis indicates roughly the empirical formula $5MgO.\ 4CO_2.\ 4H_2O$. Because it had been noted that the samples under investigation were alkaline to phenolphthalein it was thought possible that the material might be soluble in carbon dioxide solution without preliminary calcination. It was found, however, that while approximately 50% (by weight) dissolved quite readily, the remainder was attacked very slowly.

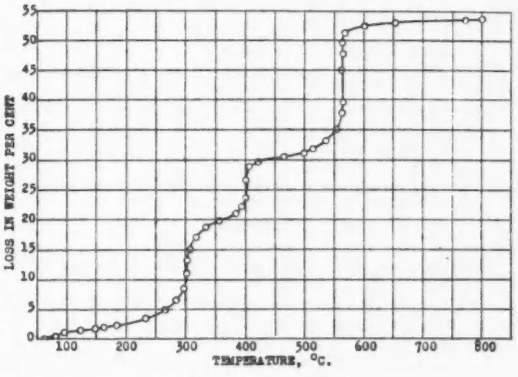

FIG. 2. *Hydromagnesite.*

The decomposition curve (Fig. 2) indicates positively two stages of evolution of carbon dioxide, *i.e.*, the higher one extends from 29% loss to 52.3%; the lower one presumably involves 13.2% carbon dioxide, which, however, in this curve cannot definitely be distinguished from water. Such a mechanism of decomposition would not agree with the empirical formula suggested above. It does, however, tend to substantiate the conclusion that this particular sample of hydromagnesite consisted of approximately 52% of a basic carbonate of the formula $3MgCO_3.\ 2Mg(OH)_2.\ 6H_2O$ mechanically mixed with an equal weight of normal carbonate, together with siliceous and other impurities. This matter was not considered sufficiently important for further investigation although light might be thrown upon it by microscopic studies. It might be observed that the accepted vapor pressure data for magnesium carbonate correspond with a decomposition temperature of approximately 550° C. The fact that the magnesium carbonate component of hydromagnesite decomposes at a temperature much closer to 550° C. than do the rock samples may be ascribed to the amorphous nature of the former which occurs naturally in a finely divided form.

Serpentine

Fig. 3 shows the thermal decomposition of a specimen of serpentine rock. The type of serpentine used in this determination occurs as an impurity in the magnesitic dolomite reported above. It will be noted that evolution of combined water occurs at a temperature substantially the same as that of the carbon dioxide of magnesite. This result was of interest in accounting for the fact that in the selective calcination of magnesitic dolomite in a commercial kiln the calcines always contained upwards of 0.5% water even when particular care was taken to eliminate air slaking during and after sampling. The evidence is that this represents residual water from undecomposed serpentine. This particular sample of serpentine was not very pure, as is shown in Table I. On the basis of the silica content it would contain 82.6% pure $3MgO.2SiO_2.2H_2O$, the balance being largely dolomite. Actually, however, there is some 1.3% more combined water than corresponds to this formula. Any carbon

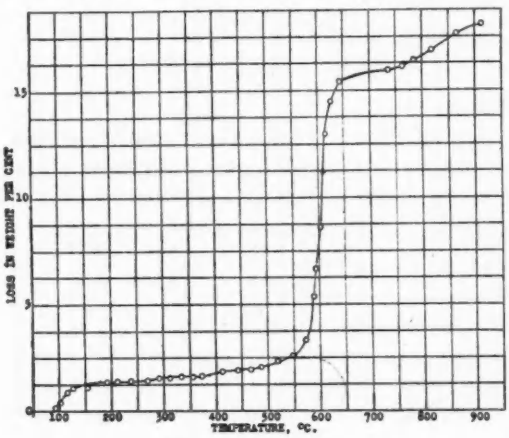

FIG. 3. *Serpentine.*

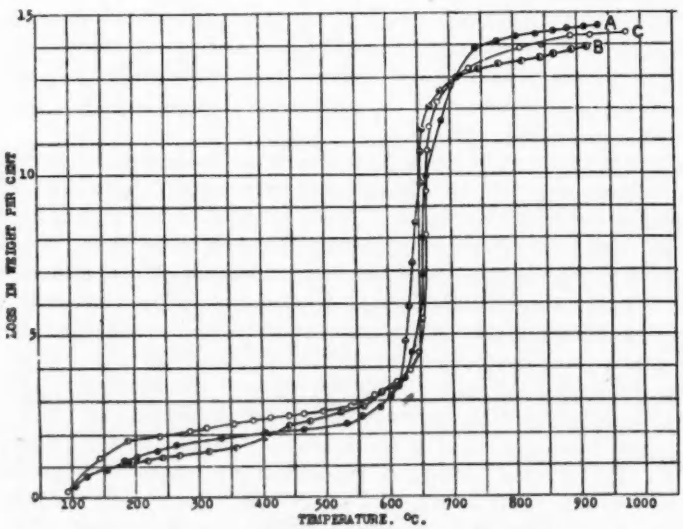

FIG. 4. *Asbestos. A, Arizona crude; B, Canadian spinning stock; C, Russian crude.*

dioxide existing in magnesium carbonate would be indistinguishable from the water of the serpentine in the decomposition curve.

Asbestos

In Fig. 4 decomposition curves are given for three different asbestos samples. As might have been expected, they are in rough agreement with the curve for serpentine rock. The dehydration of asbestos fibres is accompanied by loss of pliability and it thus destroys one of the most desired characteristics of the material. It is of interest to note that the Canadian crysotile material and Arizona and Russian crudes all undergo decomposition at substantially the same temperature. No explanation is offered for the apparent secondary decomposition of the Canadian material at approximately 400° C. The same break in the curve at this temperature was obtained in tests of three different samples of this material, indicating that it was not due to experimental inaccuracy. Two samples of African asbestos were also tested. The results, however, were unsatisfactory owing to its relatively small water content, coupled with the fact that weight losses were masked by oxidation of ferrous iron which is present in relatively large amount.

The analyses, which are reported in Table I, show the materials to be all of the serpentine type although, like the serpentine, they tend to be higher in water content than the pure compounds.

Calcium and Magnesium Hydroxides

The decomposition temperatures are shown in Fig. 5. While somewhat indefinite, they are useful approximations. The indicated point for magnesium hydroxide is approximately 375°–380° C., and that for calcium hydroxide 520–525° C. These materials were prepared in the laboratory by calcining and rehydrating chemically pure hydroxides. The water contents of pure calcium and magnesium hydroxides are respectively 24.3 and 30.9%.

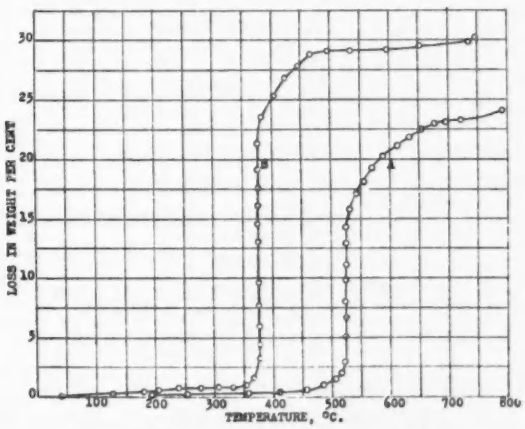

FIG. 5. *Calcium and magnesium hydroxides. A, calcium hydroxide; B, magnesium hydroxide.*

Gypsum

The material reported here was of the massive variety, it having previously been found that the points obtained with the crystalline form (selenite) were not as sharply defined. The two stages of decomposition are shown quite distinctly in Fig. 6, although the proportion in each stage is not definite

owing to the temperature lag. In commercial calcination of gypsum, the first "boil", or loss of 75% of the water, is considered to occur at 120–130° C., and the second at 180–195° C. These determinations show the more definite points of 118° and 192–193° C. respectively for the two "boils". Numerous investigations have been made of the decomposition of gypsum. Stumper (1) obtained values varying from 125–127° to 140° C. for the lower temperature and 190–192° C. for the higher.

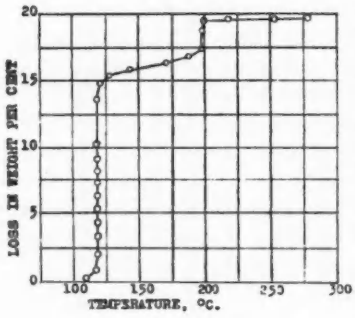

FIG. 6. *Gypsum.*

Magnesium Sulphate

The laboratory sample used was the heptahydrate of reagent grade. The curve (Fig. 7) is of interest in showing the two stages of dehydration. The temperature of 110° C. corresponds with the loss of six molecules of water, the remaining molecule coming off at approximately 350° C.

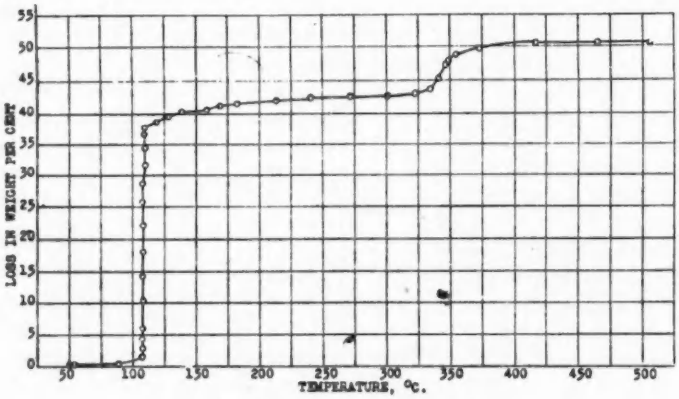

FIG. 7. *Hydrous magnesium sulphate.*

This information was used in a study of the transfer of water from crystalline magnesium sulphate to plastic magnesia, when the former was added as a neutralizing agent for free lime.

Aluminium Chloride, Hydrous

The thermal decomposition of hydrous aluminium chloride to yield a residue of aluminium oxide is well known. In connection with a study of certain proposed methods of dehydration, it became desirable to have accurate data on the temperature at which this decomposition actually takes place. This curve (Fig. 8) shows the decomposition point very satisfactorily. It is of interest also to note that the temperature, 182° C., coincides with the accepted boiling point for anhydrous aluminium chloride. The sample used

was of reagent grade. The break in the curve shortly above 100° C. is evidently due to loss of hygroscopic water.

Pyrite

Some attention is being given in this laboratory to the recovery of elemental sulphur from Canadian pyrite ores and mill tailings. This has involved consideration of the thermal decomposition of pyrite which takes place approximately according to the equation, $FeS_2 = FeS + S$. This determination was made in order to give more accurate information on the temperature of this reaction.

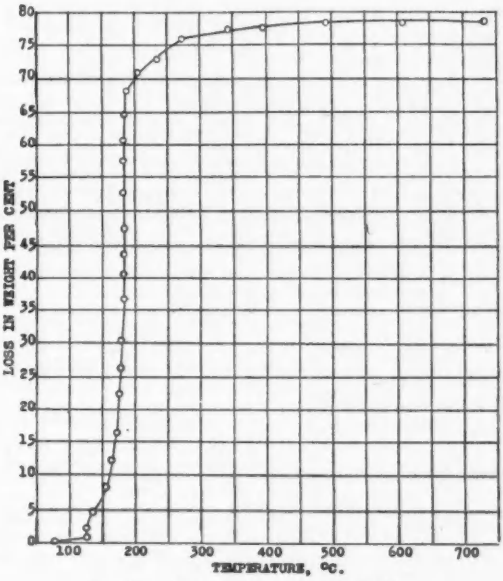

FIG. 8. *Hydrous aluminium chloride.*

In the curve (Fig. 9), the loss in the vicinity of 100° C. indicates moisture. Unfortunately no determination of moisture was made on the sample actually used. The break in the curve at approximately 8% loss indicates two stages of decomposition but no accurate indication of the intermediate product can be obtained from these data. At any rate, it is evident that the major decomposition is complete at 680–685° C.

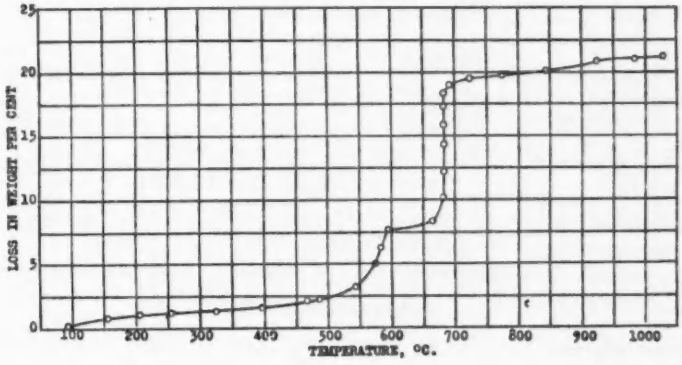

FIG. 9. *Pyrite.*

Coal

As a matter of interest, results are shown in Fig. 10 of tests on three samples

of western Canadian coals. The curves indicate the characteristics of the various materials to some extent. The data in general are an indication that this method is useful in presenting a quick picture of the moisture content together with the range over which the volatile organic matter is distilled. It is to be noted that the reported proximate analyses do not agree with the test results, owing largely to differences in the water content. Calculations on the dry basis show fair agreement when the arbitrary nature of the determination of volatile matter is considered.

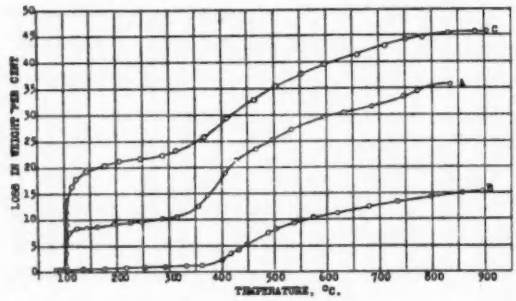

FIG. 10. *Coal samples.*

TABLE III

ANALYSES OF COAL SAMPLES

—	*A*	*B*	*C*	—	*A*	*B*	*C*
Moisture, %	10.3	1.4	18.7	Volatile matter, %	33.0	17.5	31.0
Ash, %	5.7	3.7	4.8	Fixed carbon, %	51.0	77.4	45.5

TABLE IV

INDICATED DECOMPOSITION POINTS

Substance	Decomposition point, ° C.	Substance	Decomposition point, ° C.
Magnesite	650 (max.)	Asbestos	625–660
Hydromagnesite		Calcium hydroxide	520–525
(a) Water (?)	300 (max.)	Magnesium hydroxide	375–380
(b) Carbon dioxide	400 (max.)	Gypsum	118 and 192–193
(c) Carbon dioxide	565 (max.)	Magnesium sulphate (hydrous)	100–110 and 330–350
Dolomite		Aluminium chloride (hydrous)	182
(a) CO_2 from $MgCO_3$	725	Pyrite	680–685 (max.)
(b) CO_2 from $CaCO_3$	912		
Serpentine	600–625		

Acknowledgment

Acknowledgment is made to Mr. C. W. Davis of these laboratories, who made a number of the analyses and performed some of the tests.

Reference

1. STUMPER, R. Compt. rend. 184 : 970-972. 1927.

HYSTERESIS IN SILICA GEL SORPTION SYSTEMS[1]

By L. M. Pidgeon[2]

Abstract

The hysteresis which normally appears in the isotherms of the silica gel-water system has been attributed by Patrick to the presence of permanent gases in the system. Only one case has been found in which a reversible isotherm has been recorded in the silica gel-water system. For alcohol and benzene only one case of hysteresis has been reported. These results seem to be independent of the presence or absence of air or other gases.

The sorption of water, benzene and ethyl alcohol has been examined using the sorption balance. A hysteresis loop appears for water only. This hysteresis may not be eliminated by special methods of evacuation and must be considered as a real effect. The isotherms of alcohol and benzene, on the other hand, are completely reversible. It has been shown that the dimensions of the hysteresis occurring in the water system may be affected by the manner of addition of vapor to the apparatus. Only when the vapor pressures remain reasonably constant during sorption are the dimensions of the effect evident. If very large pressure changes take place the hysteresis may disappear.

A comparison of the isotherms for water showing hysteresis, and those of the sulphur dioxide system (upon which the original suggestion as to the cause of hysteresis was based) show that there is not necessarily any relation between the two.

Introduction

The early workers on the sorption of water by silicic acid gels invariably reported isotherms in which the equilibrium values obtained by sorption from lower pressures were not as high as those obtained by loss of water from a more saturated condition. A hysteresis loop of characteristic shape was thereby produced which has been the subject of much subsequent discussion and for which a satisfactory explanation is still lacking.

More recently Patrick (9) and his collaborators, who have been responsible for much of the later work on sorption by silica gel, suggested that this hysteresis has no real existence and is simply due to the incomplete removal of permanent gases from the sorbent. This explanation of the phenomenon, based on experiments carried out on the sorption of sulphur dioxide by silica gel was extended to embrace all cases of sorption hysteresis (10, p. 1278), and as such has been accepted by a number of workers in this field (7, p. 184).

On the other hand it has been questioned, in the case of water at least, and considerable evidence produced to show that the hysteresis is a real effect and not connected with experimental error.

In this paper it is the author's intention to discuss the evidence for and against the conclusion that hysteresis is due to traces of permanent gases, and to present the results of experiments which have been carried out on the sorption by silica gel of the vapors of water, ethyl alcohol, and benzene, with special reference to the occurrence of hysteresis in the isotherms of these systems.

[1] *Manuscript received March 29, 1934.*
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Discussion

van Bemmelen (17), and Anderson (1) were among the first to examine the sorption of water vapor by silica gel. They employed the static method of measurement using sulphuric acid solutions of known strength to produce a constant vapor pressure in their apparatus. van Bemmelen's experiments were carried out in the presence of air, while Anderson used a vacuum method, although the conditions were such as to prevent very complete removal of inert gases. In all cases the characteristic hysteresis loop appeared in their isotherms.

Subsequently Patrick (12) using the dynamic method in air produced a similar hysteresis loop, although alcohol and benzene under the same conditions yielded reversible isotherms.

However Patrick (9) had already carried out the experiments on the silica gel–sulphur dioxide system, upon the results of which were based his conclusions regarding the cause of the hysteresis. In this work it was clearly shown that if small amounts of air were introduced into a thoroughly evacuated static sorption system, a hysteresis appeared which had not been present before and which could be removed by rigorous evacuation of the sample. This result seemed quite definite, and the suggestion was made that the explanation could be extended to include all cases of hysteresis. The application of such a suggestion to sorption by organic fibres was adversely criticized by Urquhart (16), who at the same time questioned its applicability to the case of silica gel itself, and turned his attention to this system. Using a static method he reported the familiar hysteresis loop for water and silica gel even after very careful evacuation technique. Whereupon Patrick (11) again examined the sorption of water, this time using a static method and taking special precautions to ensure removal of inert gas. (The samples were heated to 350° C. and evacuated a number of times and in the intervening periods were allowed to sorb water at 20° C. The isotherms which were obtained after this treatment were perfectly reversible and showed no trace of hysteresis. These results were regarded by the author as conclusive proof of his previous contention.

More recently, however, Lambert and Foster (6) examined the water-silica gel system and, in spite of the fact that they employed even more careful methods of evacuation than Patrick, and used a much more compact apparatus, a definite hysteresis loop made its appearance in their isotherms.

Similar confusion is to be found in the results of experiments on the sorption of the vapors of alcohol and benzene. Anderson (1) described a hysteresis loop in the isotherms of both of these systems which was similar in shape to that of water. On the other hand, Lambert and Clark (5) using the same elaborate evacuation technique as for the water system, found no hysteresis in either case. McBain (7, p. 188) reproduces the isotherms of both of these authors as examples of the differences which follow when evacuation is thorough. Referring to Patrick's experiment on the water

system in which the isotherms were reversible, he states that, "Lambert and Clark have performed a similar service for the isotherms of benzene and silica gel." Uncertainty again arises when it is remembered that Patrick (12) had already demonstrated that when the vapor is carried over the sorbent in a stream of air, water produces a hysteresis but alcohol and benzene do not, while as already mentioned, Lambert and Foster (6) applying the same technique they had used with benzene found a hysteresis in the case of water sorption.

It appears that the mass of evidence suggests that a real hysteresis loop appears in the isotherms of the water-silica gel system, while the isotherms of alcohol and benzene are perfectly reversible. Only in the static experiments of Patrick (11) have perfectly reversible isotherms appeared for water sorption and only one author (1) has found hysteresis in the case of benzene and ethyl alcohol. The appearance or disappearance of the hysteresis loop in these cases is apparently independent of the presence or absence of air or other gases.

Considerable importance has been attached to this experiment of Patrick's on the water-silica gel system by McBain (7, p. 185) who states, "It is most interesting to observe that the form of these isotherms for water in the absence of air and volatile impurities differs wholly from those previously obtained and resembles ordinary isotherms for charcoal. . . . To the author, it appears probable that if the drastic methods of evacuation discussed in Chap. IV were here available, the sorption isotherms would approach in form those developed for charcoal by means of the sorption balance, practically all the sorption taking place at extremely low pressures. The incompatibility of such behaviour with the hypothesis of sorption as capillary condensation has already been mentioned."

The establishment of the true position of the phenomenon of hysteresis is therefore a matter of some theoretical importance as its presence, if established, will present a fact which must be accounted for in any theoretical explanation of the mechanism of sorption.

Possible Causes of the Disappearance of Hysteresis in Certain Cases

The experiments of Patrick which showed no hysteresis are of sufficient importance to warrant detailed attention. It seems from the survey which has been made that in the case of water, the hysteresis may not be removed by careful evacuation, and the analogies which have been drawn with benzene and alcohol are incorrect. Some other cause for the disappearance of the loop must be found. The author believes that this may be discovered in the experimental method which was employed by Patrick in this particular research.

While no numerical values are given for the sorption results (11), some details of the apparatus appear. It is mentioned that 1200 cc. of gel was divided into 12 samples, each being enclosed in a suitable bulb and all connected through suitable mercury "cut-offs" to a pump, manometer and water reservoir. After evacuation, as previously described, the apparatus was filled

to various pressures with water vapor and a bulb sealed off at each measured point. The moisture content of the gel in each bulb was accurately determined by several methods. The points to which attention must be drawn are, first, that a very large amount of gel was present in the sorption system, and, second, that the alteration of vapor pressure was apparently achieved by direct addition or removal of water vapor. It is suggested that these two factors have been responsible for the disappearance of the hysteresis in these experiments.

It has been pointed out by Seborg and Stamm (15), and also by Campbell (2), that when the amount of vapor is controlled by admitting or withdrawing small amounts from a sorption system, an error is introduced when hysteresis is under examination. This is due to the fact that the direct addition of vapor to the system raises the pressure above the equilibrium value, so that the subsequent sorption takes place under a falling vapor pressure. Under these circumstances, while the system as a whole would move from an equilibrium at low vapor pressure to one at higher vapor pressure, in certain portions of the gel the process might be reversed. The more accessible parts of the sample might quickly come to equilibrium with the higher pressure of the newly admitted vapor, hence in the later stages of sorption these portions would approach equilibrium by *loss* of vapor, while the rest of the sample is gaining it. Hence the process of sorption and desorption would be taking place simultaneously. The reverse effects, of course, take place on a descending isothermal; as the vapor pressure surrounding the sample is lowered below the final equilibrium value and rises to it as equilibrium is reached.

It will be apparent that if these pressure changes are very marked there will be a possibility that, should a hysteresis exist, its presence might be obscured by the confusion of sorption and desorption, for it is conceivable that the amount of each process taking place simultaneously might exactly balance and a reversible point appear in the resulting isotherm.

The magnitude of this obscuring effect will obviously depend on pressure change which takes place during the establishment of equilibrium at any given pressure. This in turn depends to some extent on the size and nature of the gel particles, but more particularly on the ratio existing between the amount of vapor taken up by the sample between successive points and the amount of vapor in the free space of the sorption system. The greatest changes follow when a large amount of gel is enclosed in an apparatus of small free volume, while in an apparatus of large volume the fall in pressure brought about by removal of vapor by a small sample will not be large and the error from this source will be minimized. Very slow addition of vapor also reduces the error as the pressure in the system is not raised far above the new equilibrium point. Campbell and others have eliminated all uncertainty on this point by maintaining a constant vapor pressure in the system by the use of solutions of the appropriate strength.

If the experimental method of Patrick is examined in the light of this suggestion it will be found the conditions holding were particularly unfavor-

able. The method which was employed to determine the moisture content of the gel, while very accurate, necessitated the use of an unusually large amount of gel, so that the ratio of gel to apparatus was very great (1200 cc. of gel was originally present, which compares with 14 gm. in Lambert's apparatus and 2 gm. in the experiments to be described later) and the pressure changes might well be sufficient to obliterate the hysteresis.

This same criticism may be applied to the experimental methods which have been employed by a number of investigators, and in general applies to the "standard sorption method" (7, p. 12), but in no case under discussion were the conditions as unfavorable as in that referred to.

Further evidence in favor of this suggestion is found in the work of Lambert and Clark (5). These authors employed a method in which a pressure change of approximately 2 cm. of mercury existed between the vapor in the reservoir and that in the sorption system during admission of vapor. This pressure change was approximately equal to a change in p/p_s of 10%, and was not sufficient to hide the hysteresis, though its dimensions may be affected (see Figs. 4 and 7). While the characteristic loop appeared for water sorption, the authors observed that its dimensions could be altered by the manner of addition of vapor to the system. It was found that where the descending and ascending isothermals coincided, the manner of addition of the vapor produced no effect on the sorption values, but over the region where hysteresis appeared, interruptions in the admission of vapor produced points lying within the loop. "By these interruptions of smooth addition or withdrawal of benzene, it was possible to obtain equilibrium values within the hysteresis area . . . The ascending isothermal, obtained by smooth successive additions of benzene to the reaction system set an upper limit to the equilibrium pressures just as the corresponding "descending" isothermal set a limit to the equilibrium pressure."

(These observations were first made by Lambert and Clark (5) on the system ferric hydroxide–benzene which shows a similar hysteresis to that of water and silica gel. They were later repeated by Lambert and Foster (6) in the latter system.)

The interruptions referred to consisted in adding a known amount of vapor to the system, after which a portion was withdrawn. The sorption value obtained in this way was higher than that which would have appeared if the point had been reached by sorption in a regular way from a lower saturation point. It will at once be observed that this is actually what happens when a gel sorbs vapor in a closed system without special means to ensure a constant pressure. As the gel takes up the vapor the pressure in the system falls exactly as if a portion had been withdrawn by a pump or other agency as described by Lambert and Clark. Hence when hysteresis appears its true dimensions will be apparent only when the vapor pressure during the addition of vapor to the system does not rise above the equilibrium at the new point.

The remaining part of this paper describes experiments which have been carried out to test the validity of these suggestions. Experimental methods

have been adopted in which the amount of pressure change taking place during sorption may be varied, and the effect on the hysteresis of this variation studied.

Experimental

The McBain-Bakr sorption balance has been employed exclusively, as it is the most convenient method of measurement in which the determination of the amount of sorption is independent of the pressure of the vapor or the amount of liquid in the reservoir. The method of admission of vapor, and the pressure changes taking place during sorption may therefore be varied at will without affecting the sorption determination.

Apparatus

The general appearance of the apparatus is apparent from Fig. 1. The samples were placed in light buckets constructed of aluminium gauze and suspended from the spirals as indicated. The quartz springs were constructed as previously described (14). Extensions were measured with a cathetometer. The weight of the sample was determined with an accuracy of 0.1% except where otherwise stated. In order that various organic solvents could be examined, all stopcocks were eliminated and their place taken by mercury "cut-offs". The ground joints over the sample tubes were used satisfactorily in the dry condition with mercury seals. The system was evacuated with a high speed, two stage, Gaede diffusion pump backed by the customary oil-immersed mechanical pump. Pressures during evacuation were measured with a McLeod gauge, and the vapor pressure during sorption was measured on the manometer, readings being made with the cathetometer.

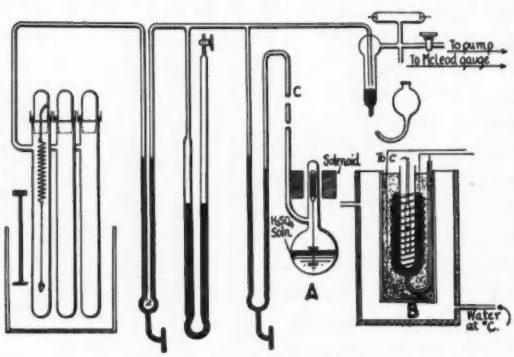

FIG. 1. *Sorption balance modified for production of constant pressures in the system.*

The general operation of the balance is obvious from the diagram. The special features having to do with the admission of vapor, pressure control, and the precautions taken to ensure the removal of permanent gases from the system will be described in subsequent sections, together with the results obtained with each method.

Materials

Commercial silica gel (−8 to +14 mesh) was employed in all experiments. The gel was obtained from two sources, the samples from each showing the same general results with small differences in the actual sorption values. The

gel was placed in the apparatus as received and in most cases was not heated prior to sorption. Pure benzene (Schuchardt) and absolute ethyl alcohol were employed in the sorption experiments on these substances.

Experimental Results

I. Sorption of Water Vapor

(a) Sorption During Constant Pressure

If the suggestions which have been set forth in the preceding section are correct, the true dimensions of the hysteresis should appear only when sorption takes place with a constant vapor pressure in the free space of the sorption system. This has been achieved in two ways:

1. Sulphuric Acid Solutions

The details of this method are shown in *A*, Fig. 1, and are in general similar to those described by Campbell (2). The constant vapor pressure of water was obtained by the use of sulphuric acid solutions of suitable concentrations immersed in the same thermostat as the samples (shown separately in diagram). A stirrer, operated by a solenoid, continually broke the liquid surface during the course of an experiment.

One litre of solution was used, so that with the average weight of sample which was employed, the change in relative humidity resulting from alteration in acid strength during sorption did not exceed 0.008%. This change in humidity is approximately equal to a temperature change of 0.01° C., which corresponded to the limit of accuracy of temperature control.

The samples were evacuated until no gas was given off and their weight determined by reading the extension of the spirals. They were then "washed" with water vapor, followed by evacuation, this process being repeated several times. The acid solution was then placed in communication with the samples and 24 hr. was allowed to elapse before taking the final reading, the solution being stirred throughout this time. The vapor pressure in the apparatus was then raised to a higher level by admission of water vapor from a separate reservoir, after which a descending point was obtained by again placing the samples in communication with the acid solution for 24 hr., after which the solution was diluted by the addition of freshly boiled distilled water and the above process repeated at a higher vapor pressure.

2. Thermostatic Control

The above method, while giving accurate control of the vapor pressure and having the sanction of previous investigators, suffered from two serious faults. The operations required to pass from one point to another on the isotherm were tedious, while the frequent opening of a part of the apparatus required by admission or withdrawal of sulphuric acid or water, rendered it difficult to ensure complete removal of permanent gases.

To obviate these difficulties the apparatus was modified as shown in *B*, Fig. 1. The control of vapor pressure was then effected by accurately main-

taining a known temperature around a water bulb placed in communication with the sorption system. A special thermostat previously described (14) was employed in this connection. Ice water was circulated through the jacket enabling constant temperatures as low as 4° C. to be maintained in the water bulb. The temperature fluctuations with this apparatus were barely detectable with a Beckmann thermometer and were unlikely to be greater than 0.005° C. With this arrangement the constancy with which the relative humidity within the apparatus may be maintained depends on the accuracy of temperature control of this thermostat and that surrounding the samples. The latter was equipped with a specially sensitive thermoregulator which gave regulation to better than 0.01° C., so that variations of relative vapor pressure were well below the accuracy of sorption determination.

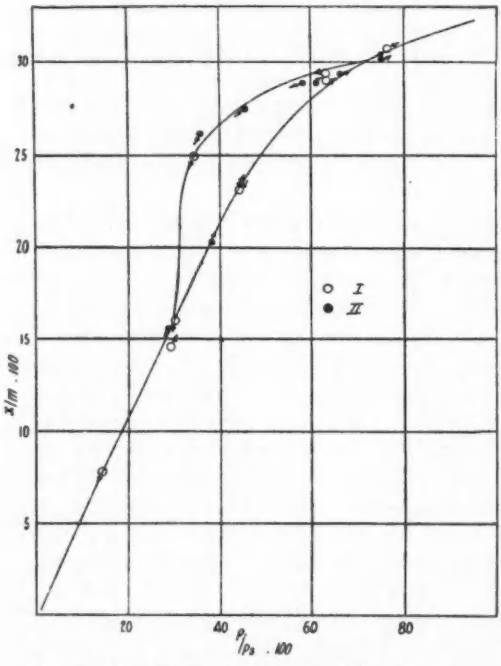

FIG. 2. *Sorption of water vapor by silica gel; constant pressure during sorption. T=20° C.*

With this modification of the apparatus it was possible to remove dissolved gases from the water by freezing and evacuation in the ordinary manner, while the various vapor pressures required for the production of the complete isotherm were readily obtainable by adjustment of the temperature of the thermostat. The temperature of each thermostat was checked with standard thermometers and the ratio p/p_s obtained from tables.

Experimental Results

Results of experiments carried out with constant vapor pressures during sorption are given in Table I and appear in Fig. 2, where "x" is the weight of water sorbed and "m" the weight of the sample. The points are identified as ascending and descending according to the direction of the vapor pressure change which has taken place.

It is at once apparent that the characteristic hysteresis is present in both cases. This type of loop is identical in shape with that reported by the various authors referred to in the introduction. Various samples of gel showed the same effect, though the actual values might be somewhat different, as seen in Table I.

TABLE I

RESULTS OF EXPERIMENTS AT CONSTANT VAPOR PRESSURES

Apparatus A. Temp., 20° C.						Apparatus B. Temp., 20.38° C.					
	Silica gel			Silica gel			Silica gel			Silica gel	
$p/p_s \cdot 100$	No. 1	No. 2	$p/p_s \cdot 100$	No. 1	No. 2	$p/p_s \cdot 100$	No. 1	No. 2	$p/p_s \cdot 100$	No. 1	No. 2
	$x/m \cdot 100$			$x/m \cdot 100$			$x/m \cdot 100$			$x/m \cdot 100$	
Ascending points			*Descending points*			*Ascending points*			*Descending points*		
29.0	14.6	14.5	76.7	36.7	30.7	44.8	24.6	23.4	63.4	34.8	29.8
44.1	24.5	23.1	63.5	35.1	29.3	60.8	30.9	28.9	58.0	33.7	28.8
63.4	33.8	28.9	34.4	26.1	24.9	66.1	34.7	29.3	45.4	32.7	27.5
76.7	36.7	30.7	29.9	14.8	15.9	75.1	35.3	30.1	35.6	29.3	26.1
			14.2	7.9	7.8				28.6	14.3	15.5
									Ascending point		
									38.4	20.2	20.2

(b) Sorption After Thorough Evacuation

In view of the very thorough evacuation employed by Patrick and others, a criticism might be leveled at the above work on the grounds that the samples were not heated during evacuation, while temperatures up to 440° C. had been employed by various authors. In order to investigate this point a special form of the sorption balance was constructed as illustrated in Fig. 3. The apparatus was constructed of Pyrex glass and the dimensions were kept small so that all parts could be heated by a free flame during evacuation. The "cut-offs" were of small size and completely enclosed and the mercury was boiled during evacuation. The manometer was constructed according to the recommendations of Lambert and Clark (4). The boiled water was introduced into tube *B* and frozen twice with evacuation before being distilled into the tube *A* and sealed off at *C* as shown. The freezing and thawing during evacuation was then repeated. The pumping system was operated until a zero reading was obtained on the McLeod gauge, after which the apparatus was tested for gas tightness over a period of several days. A sample of silica gel was placed in a glass bucket and suspended from a specially sensitive spiral (1 part to 10,000) by a fine glass thread. The following operations (i and ii) were then repeated three times:

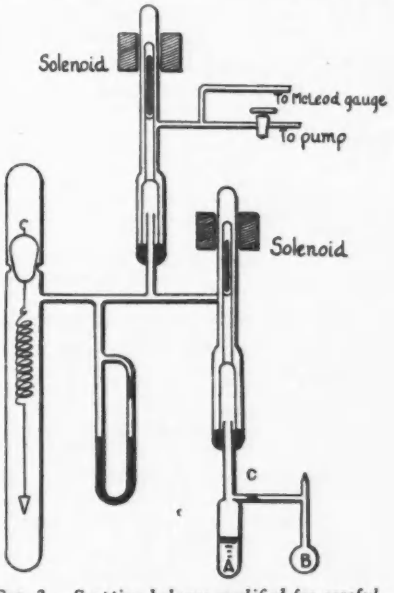

FIG. 3. *Sorption balance modified for careful evacuation of samples.*

(i) The gel was heated with a jacket furnace to 300° C. evacuated to the limit of the gauge. (ii) The gel was cooled to 20° C., and water vapor admitted; the vapor pressure rose to 4–10 mm. After this treatment the sorption points were taken in the ordinary manner, 24 hr. being allowed for the establishment of equilibrium in the case of the points falling within the hysteresis loops; longer times up to several days made no difference in the readings.

The vapor pressure during these experiments was not absolutely constant during the establishment of equilibrium, but the ratio of gel volume to free volume of apparatus (0.5 gm. of gel employed) was such that this change was very small and unlikely to affect any hysteresis which might be found. The results which appear in Table II and in Fig. 4, *B*, show the same loop as the previous isotherms. In fact the loop is even wider than those appearing where the evacuation methods had been less elaborate. The treatment has not affected the hysteresis, though the actual sorption values have been reduced by the heating. Actually, while the values are lower than those found previously the curves are affine except for a portion of the loop. It may be mentioned that no attempt was made to exclude mercury vapor from the apparatus, as it was apparently present in Patrick's experiment.

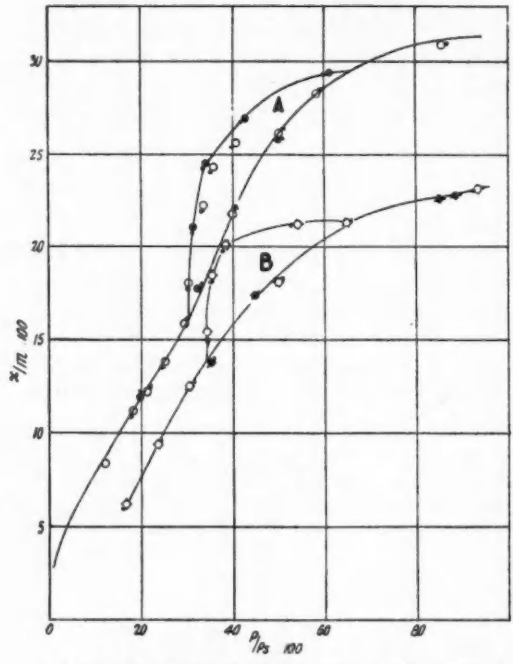

FIG. 4. *Sorption of water by silica gel. A, small pressure variations; B, sample rigorously evacuated.*

TABLE II

SORPTION OF WATER BY SILICA GEL AFTER THOROUGH EVACUATION (TEMP. 24.0°C.)

p/p_s . 100	x/m . 100	p/p_s . 100	x/m . 100	p/p_s . 100	x/m . 100	p/p_s . 100	x/m . 100
Ascending points		*Descending points*		*Descending points*		*Ascending points*	
42.6	15.1	54.2	21.2	34.2	15.4	23.5	9.3
50.0	18.1	38.3	20.1	30.6	12.5	35.5	13.8
64.8	21.3	35.3	18.5	23.8	9.4	44.8	17.4
93.2	23.1			16.2	6.2	85.0	22.6
						88.2	22.8
						Descending point	
						36.5	18.6

(c) Attempts to Remove the Hysteresis by Pressure Changes During Sorption

It appears from the foregoing that if a reasonably constant vapor pressure is maintained during the sorption of water by silica gel a characteristic hysteresis loop is formed by the curves of ascending and descending points. This loop may not be removed by special methods of evacuation as has been stated. This result is in accord with the findings of Urquhart, Lambert and coworkers, and the earlier workers on sorption of water by this substance. The suggestion has been made that the disappearance of the hysteresis in the one case in which it did not appear may have been due to the large pressure changes which took place during sorption. Experiments have therefore been carried out in which no precautions were taken to ensure the constancy of pressure during the attainment of equilibrium at any given point. The apparatus as illustrated in Fig. 1, *B*, was employed with the exception that the thermostat (*B*) was omitted and various amounts of water vapor were directly added to the apparatus after which the "cut-off" was closed, so that the vapor pressure would fall as equilibrium was reached. The results of these experiments appear in Table III and in Fig. 4, *A*.

TABLE III

RESULTS OBTAINED WITH VARIABLE VAPOR PRESSURE (SMALL PRESSURE CHANGES)

	Silica gel			Silica gel			Silica gel			Silica gel	
$p/p_s \cdot 100$	No. 1	No. 2	$p/p_s \cdot 100$	No. 1	No. 2	$p/p_s \cdot 100$	No. 1	No. 2	$p/p_s \cdot 100$	No. 1	No. 2
	$x/m \cdot 100$			$x/m \cdot 100$			$x/m \cdot 100$			$x/m \cdot 100$	
Ascending points			*Descending points*			*Descending points*			*Descending points*		
21.6	12.3	12.9	49.5	27.0	30.0	18.2	11.2	10.7	61.3	29.4	34.8
29.4	15.9	15.9	40.8	25.6	27.1	12.1	8.4	8.5	42.8	27.0	31.3
36.2	18.7	19.8	36.1	24.3	24.2	*Ascending points*			34.4	24.5	26.9
50.2	26.2	28.4	33.9	22.2	21.7	19.7	11.9	10.4	31.6	21.0	21.3
58.4	28.3	32.6	30.5	18.1	17.5	32.3	17.8	17.5			
			25.2	13.8	14.1	50.2	25.8	27.6			
						85.8	30.9	36.5			

NOTE:—*Time allowed for equilibrium 12 hr. $T=20.43°$ C.*

The hysteresis has not disappeared though its magnitude is slightly reduced. However, it will be observed that in the first cycle the highest pressure attained was 59% of saturation, and the descending points from this maximum fall within the hysteresis loop of the second cycle which was carried to a higher value, offering a further indication of the dependence of hysteresis on the manner of addition or withdrawal of vapor.

Apparently the pressure changes have not been great enough to affect the hysteresis appreciably. This was perhaps to be expected as the sorption balance, owing to the small samples which may be examined, has a much lower ratio of gel volume to apparatus volume than most of the common methods which are employed to examine sorption. (In Patrick's apparatus 1200 cc. of silica gel was initially contained in an apparatus whose volume was prob-

ably little greater than that employed in the present case where the samples totaled some 2 gm.). Steps were accordingly taken to make the conditions in this respect more comparable. A single spiral-tube was employed and 20 gm. of silica gel was placed in the bottom of the tube under the sample. With this additional sorbent in the system the amount of water vapor taken up between different points on the isotherm was about one gram. The distillation of this weight of water vapor into the system entailed a considerable rise in vapor pressure which was maintained for some time, and which later fell to the equilibrium value after closing off the water tube. In these experiments the samples were not heated during evacuation, as this process had been shown to have no effect on the results. The samples were evacuated and "washed" with water vapor as previously described.

The results appear in Table IV, together with the amount of pressure change taking place during the establishment of equilibrium at various points. In obtaining the descending points it was possible to lower the pressure to the order of a few millimetres of mercury, by operating the pump at its usual speed. When the system was isolated the pressure rose through the range indicated, as the sample lost water. It is quite apparent that the outside of the gel would become dried during the pumping process and in the later stages would approach the equilibrium by *gain* of water. There is evidence that similar conditions held in Patrick's experiment, as it is stated that "The partial pressure of water vapor over the saturated gel was reduced somewhat by pumping."

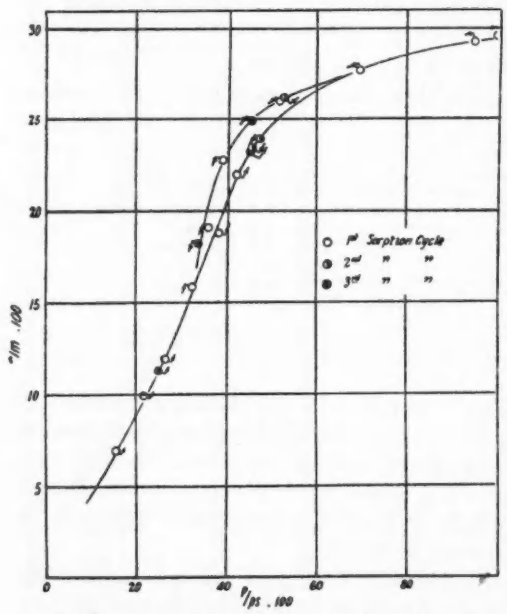

FIG. 5. *Sorption of water by silica gel; large pressure changes taking place during sorption.*

The results of Table IV appear in Fig. 5. It is apparent that the magnitude of the hysteresis has been greatly reduced, while certain points in the region of the loop are reversible, and in one case the position of "ascending" and "descending" points is reversed. While the loop has not disappeared completely in all cases, it seems fairly definite that under the correct conditions the hysteresis would become smaller than the experimental error.

TABLE IV

RESULTS OBTAINED WITH VARIABLE VAPOR PRESSURE (LARGE PRESSURE CHANGES)

p/p_s . 100	x/m silica gel	p/p_s . 100	x/m silica gel	Press. change, in mm.	p/p_1 change, %	p/p_s . 100	x/m silica gel	p/p_s . 100	x/m silica gel
Ascending points			*Descending points*			*Ascending points.*		*Ascending points*	
15.7	6.9	95.0	29.3	12.2	70	40.1	20.3	25.0	11.3
21.9	9.9	69.7	27.8	9.0	52	45.5	23.4	45.8	23.4
26.3	11.9	51.9	26.0	8.0	46	52.9	26.2	100	30.1
38.3	18.8	39.0	22.7	6.6	38	*Descending points*		*Descending points*	
42.2	21.9	35.9	19.1			47.4*	23.9	45.6	24.9
100.0	29.6	32.5	15.8					33.7	18.2
								Ascending point	
								42.2	22.2

NOTE:—*Time allowed for equilibrium 12 hr. $T=20.00°$ C.*

* *Pressure change, 8 mm.; p/p_1 change, 46%.*

Conclusions

It appears from the above that the hysteresis loop which appears during water sorption by silica gel has a real existence and is not due to the failure to eliminate air and other gases from the system. This is in accord with the findings of Anderson and other early workers on the subject, who did not take elaborate precautions to remove air from their sorption systems, and also those of Urquhart and Lambert and coworkers who carefully evacuated their samples. The reason for the disappearance of the hysteresis in the one case where it has not been reported may be due to the large pressure changes which were allowed to take place during the establishment of equilibrium, and which were of such a nature as to obscure the hysteresis. It has been possible to obtain a repetition of this behavior to a certain extent and alter the dimensions of the loop.

While from a theoretical point of view it is obvious that in any system showing hysteresis great pains must be exercised to ensure that the whole system approaches the equilibrium strictly in the direction indicated, it has been shown that very large pressure changes are required to appreciably affect the dimensions of the hysteresis—so that in most cases the precautions that were taken in this research to ensure constant pressures would not be essential.

II. SORPTION OF BENZENE AND ETHYL ALCOHOL BY SILICA GEL

It has been mentioned in the introduction that Anderson found hysteresis loops during the sorption of benzene vapor by silica gel, while Lambert and Clark later obtained reversible isotherms without trace of hysteresis. It has been suggested that this difference was due to the incomplete elimination of inert gases in the original experiments. Patrick, on the other hand, obtained reversible isotherms in the presence of air using a dynamic method.

The sorption of benzene and ethyl alcohol vapors has been carried out in the sorption balance without taking the elaborate precautions which have been recommended by Patrick and others. Samples of commercial silica gel were evacuated at room temperature after which benzene vapor was added, followed by further evacuation, this succession of events being repeated twice.

In the experiments with alcohol the gel samples were not "washed" with vapor, but were simply evacuated until no gas was given off.

The apparatus described previously (Fig. 1) was employed. The vapor pressure was not absolutely constant during sorption but the interposition of a two litre flask in the system made it nearly so, as the volume of sample employed was not greater than 2 cc., while the total volume of the apparatus was about four litres. The work on water having shown that fairly large pressure changes are required to affect a hysteresis appreciably, this degree of pressure constancy seemed adequate.

The results of these experiments appear in Tables V and VI and are plotted in Fig. 6. No hysteresis appeared in either case and the curves are in general similar to those reported by Lambert and coworkers. The benzene isotherm is notably different from that of water, in that most of the sorption takes place at low relative vapor pressures. Alcohol appears to occupy an intermediate position. The differences have been referred to by Lambert and others and will not be discussed further here. It seems quite definite that no hysteresis appears during the sorption of these vapors by silica gel and its absence is not connected with the removal of traces of inert gases, as has been suggested. Anderson reported loops for both of these sorbents which were similar in shape to those found for water but they have not been repeated in any later work.

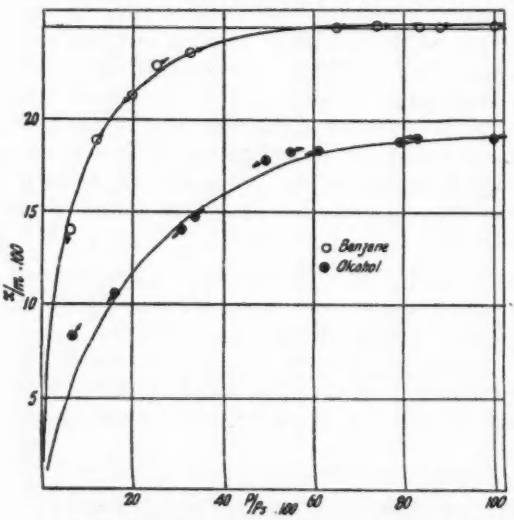

FIG. 6. *Sorption of vapor by silica gel. Isotherm bars—benzene at 20° C., and alcohol at 23° C.*

TABLE V

SORPTION OF BENZENE BY SILICA GEL (T = 20.04° C.)

Silica gel No. 1						Silica gel No. 2			
p/p_s.100	x/m.100	p/p_s.100	x/m.100	p/p_s.100	x/m.100	p/p_s.100	x/m.100	p/p_s.100	x/m.100
Ascending points		*Descending points*		*Ascending points*		*Ascending points*		*Descending points*	
32.8	23.6	83.5	25.0	11.9	18.5	31.0	23.6	43.2	25.0
65.0	25.0	19.9	21.3	25.2	22.9	45.0	25.2	15.6	21.0
74.0	25.1	6.1	14.0	65.8	24.6	62.3	25.4	*Ascending points*	
100.0	25.1			88.0	25.0	77.2	25.6	46.5	24.8.
						84.0	25.7	65.3	25.3

TABLE VI

SORPTION OF ALCOHOL VAPOR BY SILICA GEL (T = 23.00° C.)

	Ascending points					Descending points				
p/p_s . 100	6.5	33.8	54.9	79.3	100.0	83.3	61.5	48.8	30.7	16.0
x/m . 100	8:3	14.7	18.2	18.8	19.0	19.0	18.3	17.8	14.1	10.6

Conclusions

It has been demonstrated that the hysteresis which appears during the sorption of water by silica gel may not be removed by special methods of evacuation and is therefore not due to the presence of permanent gases in the system. On the other hand, McGavack and Patrick have shown that when air is present in the sorption of sulphur dioxide by silica gel, a hysteresis definitely appears which may be removed by elimination of the air.

In order to seek an explanation of the apparent contradiction the results of McGavack and Patrick have been plotted as x/m against p/p_s, rather than against pressure. A typical isotherm appears in Fig. 7 together with one from the work of Lambert and Foster on water. It is at once apparent that when the results are plotted on the same basis, there is not necessarily any relation between them, and that an explanation suitable for one may not be applicable to the other.

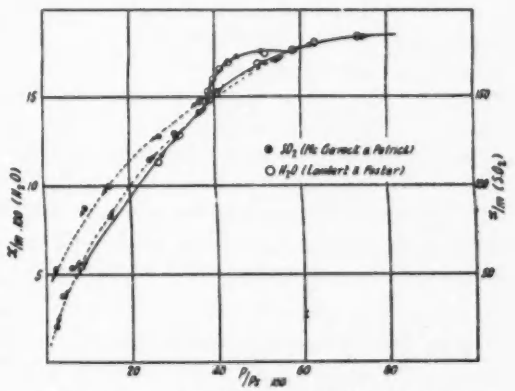

FIG. 7. *Sorption of sulphur dioxide and water by silica gel.*

These general types of hysteresis loop have been discussed by Urquhart who points out that the sulphur dioxide desorption and sorption curves are identical, but are separated by a constant distance in a direction parallel to the pressure axis, while the water hysteresis loop encloses an area of characteristic shape. Again the sulphur dioxide hysteresis extends from the origin as far as the isotherm was examined, and hence over a region where other authors obtained perfect reversibility. It is difficult to see why, if the cause of hysteresis in the water system is sorbed air, it should exert its effect in a specific portion of the isotherm. It seems that these two effects are quite separate and it is unfair to compare the two isotherms.

The comparison would probably not have been made if the isotherms had been compared only over the same portion, as in Fig. 7. That is, when the sorption of different vapors below the critical temperature are to be compared, the sorption values should be plotted against p/p_s rather than pressure. In this way it is possible to compare the amount of sorption taking place at the same fraction of the saturation pressure in the case of different vapors.

A number of other cases could be cited where a failure to emphasize this point has lead to doubtful conclusions. Patrick, Preston and Owens (13), for example, examined the sorption of carbon dioxide and nitrous oxide on silica gel. In the interests of the capillary condensation theory they investigated the sorption of these vapors above and below the critical temperature, and obtained no break in the curves. They concluded therefore that "in the pores of the gel, the critical temperature is raised, and that condensation and surface tension exist even at 40°". Actually these experiments were carried out at pressures of 650 mm. while p_s was of the order of 70 atmos. The ratio p/p_s was therefore approximately 0.01 and it is generally considered that the capillary condensation theory may not be applied below $p/p_s=0.1$ even if it is applicable at higher pressures.*

Urquhart quotes the work of Gregg (3) in this connection, pointing out the same error. This author examined the sorption of nitrogen, carbon dioxide, carbon monoxide, acetylene, ethylene, ethane and ethyl chloride; a permanent hysteresis was found only in the last case, which was then considered to be anomalous and the results were discarded. Plotting these results against p/p_s (excluding, of course, gases above their critical temperature) it will be seen that widely different portions of each isotherm were examined and only in the case of ethyl chloride was the saturation pressure closely approached—there is therefore no assurance that hysteresis might not have occurred in some other case, had comparable values of p/p_s been obtained.

In general it seems that the phenomenon is too complicated to be disposed of with the simple suggestion which has been put forward, and no entirely satisfactory explanation for its appearance or disappearance in sorption by inorganic materials has been put forward.

* *McBain and Britton (8) examining the effect of critical temperature on sorption of the nitrous oxide by charcoal, employed pressures up to 60 atmos., bringing p/p_s to reasonable limits.)*

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THE HARSHNESS OF WOOL AND ITS MEASUREMENT[1]

By P. Larose[2]

Abstract

As part of an investigation into the causes of the harshness of certain wools, an apparatus was devised by means of which the ease or extent to which wool can be compressed is measured. Four samples of yarn differing in harshness have been tested with this apparatus. The same samples were also tested by a method described by Winson. The results show that when the wools are placed in order of decreasing harshness, they are also in order of increasing compressibility; the softer the wool the more easily it is compressed.

Measurements have been made at 50% and at 60% relative humidity.

Introduction

The present study was undertaken as a result of an enquiry relating to the cause of the harshness in some wools when compared with other wools of the same fineness when spun into yarn. This difference in harshness seemed more pronounced when the wool was dyed.

The first problem was to devise a method which would permit the comparison of the harshness of various wools and to a certain degree its expression in quantitative terms. The author believes that the method described in this paper answers the purpose sufficiently well to serve as a measure of harshness.

Since the feeling of harshness is a tactual one obtained on compressing the wool in the hand or between the fingers, it seemed reasonable to suppose that the harsher wool is the one which offers the greater resistance to compression and therefore exerts the larger pressure on the hand or fingers when thus compressed.

A method then which allows the extent of compression for various pressures to be determined should serve as a measure of harshness.

A method described by Winson (4) enables what he calls the "resilience" of the wool to be measured. In that method, the resilience is measured by the area of the loop contained between the curves representing the volume-pressure relation when the wool is compressed and when it is released. When it was tried on the samples which the author had on hand, the method did not give very conclusive results and another method was devised. The results obtained by this method when analyzed as Winson has done did not appear at first to be any better than those obtained by his method. However, on analyzing the data more closely, it was found that both methods could give results from which the harshness of the wool could be determined. The author assumes that what Winson was attempting to measure was the same property, for he uses the term resilience as synonymous with springiness.

Winson used his method on raw wool samples while the wool which the author had to investigate was in the form of yarn, of which four samples were tested.

[1] *Manuscript received April 23, 1934.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

[2] *Chemist, National Research Laboratories, Ottawa.*

The yarns on the study of which the present communication is based were 4/14's of 56's quality. They were made from two different batches of wool and the yarn from one was found to be harsher than that of the other although they had undergone the same treatment in the mill as regards twisting, dyeing, etc. After dyeing, the yarn was still harsher. Four samples were consequently examined; one white and one that was dyed red, from each of the two wools. Unfortunately the source of the wool could not be traced and the breed of sheep from which the wool of one batch originated may not have been the same as that from which the other batch was obtained. The samples had however been selected by practical mill men as representing a harsh wool and a relatively soft one respectively. Moreover in the judgment of these men, the dyed yarn was in each case somewhat harsher than the corresponding white yarn. This was readily confirmed by tactual examination when the samples arrived at the laboratory.

For future reference the harsher of the two wools will be called No. 1, and the other or softer wool will be known as No. 2.

The present work will be continued with a view to correlating the results obtained by this method with other elastic properties of the wool fibre, and to determine the effect of various manufacturing operations on this property.

Apparatus

The apparatus used in the first method was the same as that described by Winson (4). The rubber balloon had a capacity of about 50 cc. and the wool was subjected to pressures up to 50 cm. of mercury.

The apparatus devised for the second method is shown in Fig. 1. It consists of a rod fixed to a solid base and on which slide three supports or brackets, *A*, *B* and *S*. These can be fixed in position by means of screws *Y*. Support *S* holds a circular knurled nut *F* threaded to receive the screw *E*, an opening in *S* being large enough to allow the screw *E* to slip through. A cylinder *C* is fixed rigidly to the screw *E* and into it is placed the sample to be tested. The actual dimensions of the cylinder used are 4.4 cm. diameter and 3.72 cm. depth. By turning the nut *F* the screw *E* with cylinder can be raised or lowered. The pitch of the screw is 1 mm. and *F* is graduated near the edge into 100 divisions so that the displacement of the cylinder can be measured to 0.01 mm. A small pointer *N* fixed to *S* enables one to read fractional turns of the nut *F* while the number of com-

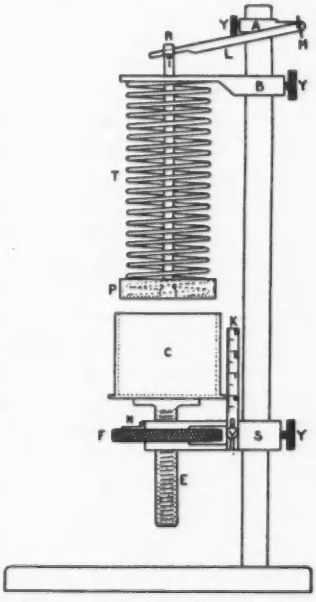

FIG. 1. *Apparatus for measuring compressibility of wool.*

plete turns are determined by noting the movement of the cylinder along scale K graduated in mm. and fixed to S by means of screw V.

The support B holds a spring T, flattened at both ends. Through B passes the rod R of the piston P which is of aluminium so as to be as light as possible. The outside diameter of the piston is a little less than the inside diameter of the cylinder in order to eliminate all friction between the two. The upper part of the rod R is slit so as to permit a thin lever L to rest on a pin I fixed through the piston rod. At the other end of the lever is rigidly fixed a pin which is free to rotate in the support A. To the pin is fixed a small mirror M with its plane parallel to the pin and at right angles to the lever. A spot of light thrown on this mirror and reflected on to a scale some distance away served as the means of determining the displacement of the piston and the compression of the spring with which the piston was in contact throughout the experiment.

The apparatus as described above involves no new principle. A helical spring for exerting the pressure has been used by Schiefer (3), and a piston and a cylinder formed part of an apparatus described by Haven (1). Haven's apparatus however was designed for large quantities of material, and that of Schiefer is not suitable for fibrous material in loose form. The present apparatus is practically free of the frictional error found by Schiefer with his apparatus, and has also been used successfully with asbestos by van Winsen*, and with other fibrous material.

Experimental Procedure

The experiments carried out by Winson's method were made under ordinary room conditions, but the experiments by the cylinder method were performed in a room where the relative humidity was maintained at 50% for one series of tests and at 60% for another, and the temperature at 70° F.

The sample of wool to be tested was placed in the cylinder after the latter had been moved to its lowest point near the zero of the scale K. The support S was then raised gently until the wool touched the piston which hung away from the spring, the pin L through the piston rod preventing the piston from dropping through the support B. The cylinder was raised further until the piston almost touched the spring. The position of the piston, as indicated by the spot of light, when in contact with the spring was determined previously by pushing up the piston lightly with the finger. The resistance offered by the spring the moment the two are in contact is readily felt by the finger. This gives the zero position for the spot of light and when once determined supports A and B should not be changed. The nut F is then set at the zero point and held there while the cylinder is rotated until the piston touches the spring, that is, until the spot of light reaches its zero position. The scale K is then so adjusted that its zero point coincides with some reference mark on the cylinder.

The apparatus is now ready for the compression of the material to be tested. It will be noted that the wool is already slightly compressed by the

* *Unpublished results.*

piston but the latter was made so light (15 gm.) that the error in the zero volume obtained by extrapolation is very small. From now on, the nut F is slowly rotated to raise the cylinder. It may be necessary occasionally to hold the cylinder to prevent it from rotating with the nut. At various intervals during the experiment the position of the spot of light on the scale is noted, while the displacement of the cylinder is also observed. This displacement is readily obtained by noting the position of the cylinder along K, and the division on F opposite the index N. In the actual experiments, a reading was taken for every 5 cm. movement of the spot of light until the total displacement was 55 cm., which corresponded to a spring compression of 1.33 cm. Previous calibration of the spring showed this to correspond to a pressure of 761 gm. for the tests at 60% relative humidity, and 792 gm. for those carried out at 50% relative humidity. The release stroke was then performed in the reverse direction, the nut being turned so as to lower the cylinder.

As in the first method described by Winson, for the first few strokes the wool does not come back to its original volume after the pressure is released, and it becomes necessary after each stroke to adjust the support S and the cylinder in order to bring the piston in contact with the spring and start from the same zero point. Generally this becomes unnecessary after the fifth or sixth stroke. In order to calculate the actual volume occupied by the wool the distance between the top of piston and bottom of cylinder had to be measured with a cathetometer once during each cycle, generally at the beginning.

The form of the samples used in the two methods was not the same. In the first method the yarn was cut in lengths of 2½ in. and the four strands were separated from one another. The method having been devised for raw wool it was thought that this procedure would, without undue work, give the wool such a form that the tests with it would approximate as nearly as possible the tests with raw wool. In the second method however no such division of the yarn was made. The necessary length of yarn, weighing about three grams, was simply folded over and over until it formed a small bundle about 2½ in. long. This was placed in the cylinder with the yarn approximately parallel to the bottom. However, care was taken that the yarn was as nearly as possible in the same condition in all experiments. For instance, the length of yarn and method of folding were exactly the same in all tests, so that the small bundle was always made up of the same number of strands.

Results

Before carrying out any compressibility tests the main dimensional characteristics which would possibly affect this property were determined. These were fibre length, fibre diameter and number of scales. The results obtained are shown in Table I. Only the undyed yarn was used.

TABLE I

DIMENSIONAL CHARACTERISTICS

—	Fibre diam.	Fibre length, cm.	Scales per mm.
No. 1	30.4μ	9.8	76
No. 2	29.9μ	12.7	72

Table II illustrates a typical set of observations obtained in the compressibility experiments with a sample of No. 2 dyed yarn at 50% relative humidity. The weight of wool was 3.28 gm. The observations for the compression stroke only are recorded.

TABLE II

A TYPICAL SET OF OBSERVATIONS

Scale reading for piston displacement, cm.	Cycle						
	I	II	III	IV	V	VI	VII
	Cylinder displacement, cm. (given by micrometer screw)						
5	0.22	0.24	0.24	0.23	0.23	0.22	0.22
10	0.47	0.48	0.46	0.46	0.46	0.45	0.45
15	0.73	0.73	0.70	0.70	0.68	0.68	0.69
20	0.95	0.96	0.93	0.93	0.92	0.90	0.91
25	1.15	1.17	1.15	1.15	1.13	1.13	1.13
30	1.37	1.37	1.34	1.34	1.32	1.32	1.30
35	1.56	1.56	1.53	1.54	1.50	1.52	1.49
40	1.76	1.75	1.71	1.71	1.69	1.68	1.67
45	1.94	1.94	1.88	1.89	1.86	1.86	1.85
50	2.11	2.10	2.06	2.06	2.04	2.01	2.02
55	2.28	2.28	2.22	2.23	2.20	2.18	2.18
Top of piston to bottom of cylinder before compression	14.41	14.39	14.32	14.31	14.26	14.26	14.26

TABLE III

RESULTS AT 50% HUMIDITY FOR THE FOUR SAMPLES OF YARN.
The figures are based on 3.25 gm. of material

Press., gm.	No. 2 Undyed		No. 1 Undyed		No. 2 Dyed		No. 1 Dyed	
	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$
Down stroke								
15	30.6	0.974	37.7	0.987	35.6	0.984	43.4	0.987
67	28.1	.895	35.8	.937	33.4	.923	41.9	.952
132	25.6	.816	34.0	.890	31.7	.876	39.8	.905
202	23.8	.758	32.2	.843	29.7	.821	38.1	.866
272	22.5	.716	30.7	.804	28.3	.782	36.7	.834
342	21.3	.678	29.3	.767	27.0	.746	35.5	.807
415	20.5	.653	28.2	.738	25.9	.716	34.3	.780
488	19.6	.624	27.2	.712	25.0	.691	33.2	.754
562	19.1	.608	26.5	.694	24.2	.666	32.2	.732
638	18.5	.589	25.8	.676	23.5	.649	31.5	.716
716	18.0	.574	25.2	.660	23.0	.636	30.7	.698
792	17.6	.561	24.5	.641	22.4	.619	30.0	.682

TABLE III—*Concluded*

RESULTS AT 50% HUMIDITY FOR THE FOUR SAMPLES OF YARN.
The figures are based on 3.25 gm. of material

Press., gm.	No. 2 Undyed		No. 1 Undyed		No. 2 Dyed		No. 1 Dyed	
	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$
Up stroke								
716	17.6	.561	24.6	.644	22.4	.619	30.1	.684
638	17.7	.564	24.7	.647	22.4	.619	30.2	.687
562	17.9	.570	24.8	.649	22.5	.622	30.3	.689
488	18.0	.574	25.1	.657	22.6	.624	30.8	.700
415	18.5	.589	25.4	.665	22.9	.633	31.1	.707
342	19.0	.605	25.9	.678	23.4	.646	31.7	.721
272	19.6	.624	26.7	.699	24.2	.668	32.5	.739
202	20.5	.653	27.5	.720	25.2	.696	33.2	.754
132	22.0	.701	29.0	.759	26.7	.738	35.2	.798
67	24.7	.787	32.0	.838	29.5	.815	38.1	.866
V_o	31.4		38.2		36.2		44.0	

TABLE IV

RESULTS AT 60% HUMIDITY FOR THE FOUR SAMPLES OF YARN.
The figures are based on 3.25 gm. of material

Press., gm.	No. 2 Undyed		No. 1 Undyed		No. 2 Dyed		No. 1 Dyed	
	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$	Vol. (V), cc.	Ratio $\frac{V}{V_o}$
Down stroke								
15	33.0	0.982	37.3	0.992	36.0	0.986	40.9	0.993
64	30.9	.920	36.0	.957	34.5	.945	39.2	.952
127	28.6	.852	34.7	.923	32.8	.898	37.9	.920
194	26.6	.792	33.4	.888	31.0	.849	36.6	.888
262	24.9	.741	32.2	.856	29.9	.819	35.4	.859
329	23.6	.702	31.0	.824	28.6	.784	34.4	.835
400	22.3	.664	29.9	.795	27.3	.748	33.3	.808
470	21.5	.640	29.1	.774	26.3	.720	32.4	.786
541	20.6	.614	28.4	.755	25.5	.698	31.8	.772
614	19.9	.592	27.5	.731	24.5	.671	31.0	.753
689	19.5	.581	27.0	.718	23.9	.655	30.4	.738
761	18.9	.563	26.3	.699	23.4	.641	29.8	.724
Up stroke								
689	19.2	.572	26.4	.702	23.5	.644	29.9	.726
614	19.4	.578	26.6	.707	23.7	.649	30.0	.728
541	19.5	.580	26.8	.712	23.9	.655	30.1	.730
470	19.7	.586	27.0	.718	24.2	.663	30.4	.738
400	20.1	.598	27.2	.723	24.5	.671	30.7	.745
329	20.5	.610	27.6	.734	25.2	.690	31.1	.755
262	21.5	.640	28.1	.747	25.8	.707	31.7	.770
194	22.5	.670	29.0	.771	27.0	.740	32.6	.792
127	24.3	.724	30.3	.802	28.6	.784	33.9	.823
64	27.2	.810	32.5	.864	31.2	.855	36.5	.886
V_o	33.6		37.6		36.5		41.2	

TABLE V

RESULTS OF TESTS BY WINSON'S METHOD

No. 1 Dyed			No. 1 White			No. 2 Dyed			No. 2 White		
Press., cm. Hg.	Vol., cc.	β/β_o	Press., cm. Hg.	Vol., cc.	β/β_o	Press., cm. Hg.	Vol., cc.	β/β_o	Press., cm. Hg.	Vol., cc.	β/β_o
Down stroke											
0.0	43.1	1.00	0.0	40.2	1.00	0.0	40.6	1.00	0.0	37.6	1.00
2.57	40.6	.941	4.76	33.9	.844	4.73	34.7	.853	4.28	31.7	.844
5.33	37.6	.873	10.69	29.0	.721	10.59	29.8	.732	10.18	26.7	.731
8.40	35.2	.817	12.29	28.2	.702	17.06	26.7	.658	16.35	23.7	.646
11.07	32.7	.760	16.80	26.3	.656	23.83	24.6	.606	22.70	21.8	.593
14.50	31.8	.737	24.30	24.7	.614	30.08	23.3	.573	29.09	20.4	.554
18.00	29.8	.692	27.18	24.0	.598	38.00	22.1	.544	37.21	19.1	.524
21.04	29.0	.673	31.13	23.3	.579	45.22	21.2	.521	44.04	18.2	.500
24.81	27.7	.643	38.64	22.1	.550	50.76	20.7	.510	47.28	18.0	.490
27.91	26.9	.625	45.72	21.2	.527				52.65	17.0	.452
34.60	25.4	.590	50.94	20.6	.514						
41.70	24.3	.564									
50.51	22.8	.534									
Up stroke											
41.28	23.1	.538	45.28	20.7	.515	44.60	20.7	.510	44.35	17.5	.465
34.08	28.6	.552	38.21	20.9	.520	34.20	21.4	.527	37.44	17.7	.470
30.24	23.6	.548	36.91	21.1	.525	29.50	21.6	.531	29.33	18.2	.483
26.68	24.4	.573	30.68	21.5	.535	23.70	22.4	.551	21.66	19.1	.509
22.85	24.8	.575	23.40	22.3	.556	19.04	23.3	.574	19.46	19.6	.522
19.59	25.7	.601	20.47	23.0	.574	15.86	23.9	.590	15.23	20.3	.541
15.89	26.4	.613	16.27	23.8	.592	13.38	24.9	.613	8.79	23.0	.612
12.47	28.0	.656	9.65	26.2	.652	9.47	26.2	.646	3.38	28.4	.755
9.73	28.9	.670	6.95	28.1	.700	6.33	28.7	.706	1.21	33.4	.890
6.16	32.1	.745	3.89	30.9	.770	3.94	31.5	.774	0.03	36.4	.970
3.83	34.5	.800	0.07	38.8	.966	1.53	36.2	.891			
0.89	40.1	.920									

The ratio $\frac{V_p}{V_{15}}$ was calculated instead of the ratio $\frac{V_p}{V_o}$. V_o was not determined as it would have to be obtained by extrapolation of the curves, which were not drawn in these cases. However the difference that would result from such a change would be very small.

The results in Tables III and IV are plotted in Figs. 2, 3, 4 and 5. In Fig. 2 are plotted the volumes occupied by the wool at various pressures and 50% humidity, and in Fig. 3 are similar results at 60% humidity. The thick lines represent the compression strokes and the light lines, the release or up-strokes. In Fig. 4 are plotted the volumes for the compression strokes only, but for the two humidities for purposes of comparison. Fig. 5 gives the ratios of the volumes at different pressures to the original volume, V_o, for the compression strokes. In Figs. 4 and 5 the dotted lines represent the results at 50% humidity, and the full lines, the results at 60% humidity.

In Table V and Figs. 6 and 7 are given the results obtained by the balloon method. In Fig. 6 the results are plotted as in Figs. 2 and 3, while in Fig. 7 they are plotted as by Winson. It is to be noted that Winson corrected for

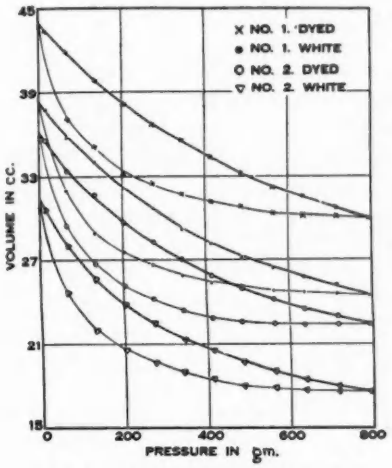

FIG. 2. *Relation between volume and pressure at 50% humidity.*

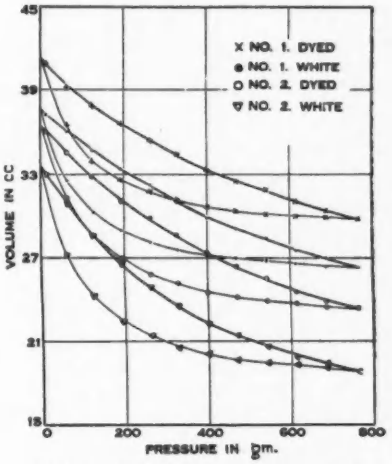

FIG. 3. *Relation between volume and pressure at 60% humidity.*

the actual volume of the wool which was subtracted from the total volume occupied by the wool to obtain the free volume. This was not done in giving the results in the above tables (Table V excepted) and in plotting Figs. 2, 3, 4 and 5. It was found that there was no advantage in doing this for purposes of comparison.

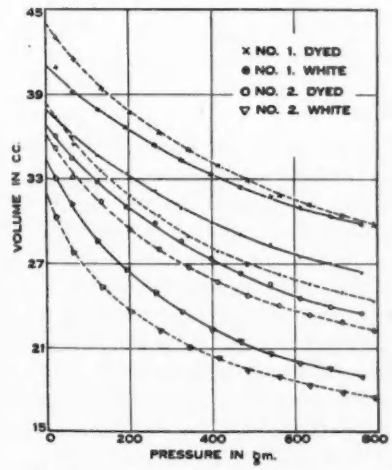

FIG. 4. *Relation between volume and pressure for down stroke. The full lines represent the results at 60% humidity, and the broken lines the results at 50% humidity.*

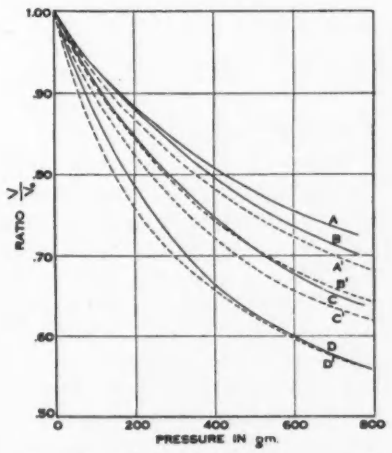

FIG. 5. *Relation of V/V_0 to pressure for down stroke. The full lines represent the results at 60% humidity, and the broken lines the results at 50% humidity. A and A', No. 1 dyed; B and B', No. 1 white; C and C', No. 2 dyed; D and D', No. 2 white.*

TABLE VI

COMPARISON OF VOLUMES OCCUPIED BY THREE DIFFERENT WEIGHTS OF WOOL
(No. 2 DYED)

Press., gm.	3.26 gm.			4.34 gm.				2.20 gm.			
	V_p, cc.	$\frac{V_p}{\text{Weight}}$	$\frac{V_p}{V_{15}}$	V_p, cc.	$\frac{V_p}{\text{Weight}}$	$\frac{V_p}{V_{15}}$	Vol. calcd. to 3.26 gm.	V_p, cc.	$\frac{V_p}{\text{Weight}}$	$\frac{V_p}{V_{15}}$	Vol. calcd. to 3.26 gm.
Down stroke											
15	35.7	1.10	1.00	47.1	1.09	1.00	35.4	28.0	1.27	1.00	41.5
67	33.5	1.03	0.94	44.5	1.03	0.95	33.5	25.8	1.17	0.92	38.2
132	31.8	0.98	0.89	42.0	0.97	0.89	31.6	23.1	1.05	0.83	34.2
202	29.8	0.91	0.84	39.7	0.92	0.84	29.8	21.3	0.97	0.76	31.6
272	28.4	0.87	0.80	37.7	0.87	0.80	28.3	19.9	0.90	0.71	29.5
342	27.1	0.83	0.76	35.9	0.83	0.76	27.0	18.9	0.86	0.68	28.0
415	26.0	0.80	0.73	34.5	0.80	0.73	25.9	17.9	0.81	0.64	26.5
488	25.1	0.77	0.70	33.1	0.76	0.70	24.9	17.2	0.78	0.61	25.5
562	24.3	0.75	0.68	32.1	0.75	0.68	24.2	16.6	0.75	0.59	24.6
638	23.6	0.72	0.66	31.2	0.72	0.66	23.5	16.1	0.73	0.58	23.8
716	23.1	0.71	0.65	30.4	0.70	0.64	22.9	15.5	0.71	0.55	23.0
792	22.5	0.69	0.63	29.8	0.69	0.63	22.4	15.1	0.69	0.54	22.4
Up stroke											
716	22.5	0.69	0.63	29.8	0.69	0.63	22.4	15.1	0.69	0.54	22.4
638	22.5	0.69	0.63	29.9	0.69	0.64	22.5	15.2	0.69	0.54	22.5
562	22.6	0.69	0.63	30.1	0.69	0.64	22.6	15.4	0.70	0.55	22.8
488	22.7	0.70	0.64	30.4	0.70	0.65	22.9	15.5	0.71	0.55	23.0
415	23.0	0.71	0.64	30.9	0.71	0.66	23.2	15.8	0.72	0.56	23.4
342	23.5	0.72	0.66	31.3	0.72	0.66	23.5	16.3	0.74	0.58	24.2
272	24.3	0.75	0.68	32.2	0.74	0.68	24.2	16.9	0.77	0.60	25.0
202	25.3	0.78	0.71	33.7	0.78	0.72	25.4	17.8	0.81	0.64	26.4
132	26.8	0.82	0.75	35.6	0.82	0.76	26.8	19.3	0.88	0.69	28.6
67	29.6	0.91	0.84	39.8	0.92	0.85	29.9	21.9	1.00	0.78	32.5

Example of Calculation

Taking the last reading of Table II for example, the cylinder was raised through 2.18 cm. while the piston's displacement was that corresponding to the 55 cm. of the scale. Calibration of the scale with the cylinder empty showed that 55 cm. of the scale was equivalent to a piston movement of 1.33 cm. The amount of compression then was $2.18-1.33$ or 0.85 cm. Since the height of the piston was 11.92 cm., the original height of the wool was $14.26-11.92$ or 2.34 cm. and after compression, $2.34-0.85=1.49$ cm. The area of the cylinder being 15.2 sq. cm., the volume of the wool after compression was $15.2 \times 1.49=22.6$ cc. The pressure at which the wool had this volume was obtained from the piston displacement, which was the same as the spring compression, and a previous calibration of the spring. The pressure for the above figures was 792 gm.

These calculations need not be done with all the readings, but only on the means for the cycles carried out after the wool has apparently reached an equilibrium, such as the last three cycles in the example given above.

Since all the samples differed slightly in weight, a correction had to be made in order to compare the results. For this correction it was assumed that the volume occupied by the wool was proportional to the weight, at least within the narrow range where the correction was applied. This was justified by some tests made with three different weights of the No. 2 dyed sample. The results of these tests are given in Table VI. The other results are given in Tables III and IV. As the weights of the samples varied around 3.25 gm. all the figures have been calculated for this weight of wool. The results are the means of three or more determinations on different samples.

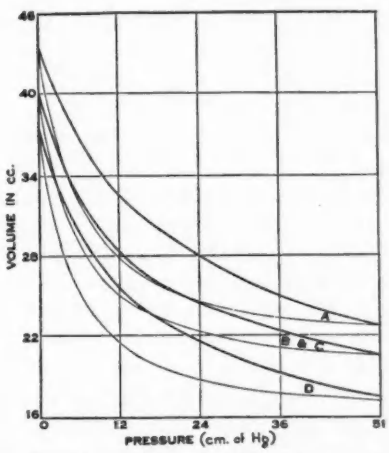

FIG. 6. *Relation between volume and pressure (Winson's method). A, No. 1 dyed; B, No. 1 white; C, No. 2 dyed; D, No. 2 white.*

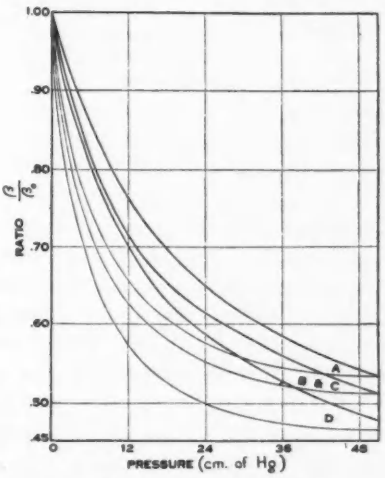

FIG. 7. *Relation between β/β_0 and pressure (Winson's method). A, No. 1 dyed; B, No. 1 white; C, No. 2 dyed; D, No. 2 white.*

Discussion

Since the samples used in the two methods were not of the same form, direct comparison is probably not justified. However the two sets of results as represented by the curves should be comparable qualitatively. It is difficult to see for example why the first method showed no difference between No. 1 undyed and No. 2 dyed yarns, while the second showed a pronounced difference. The fact that the relative humidity was not controlled in the first case may account for this. It is possible that these two samples had a different water content owing to different surrounding conditions. The cylinder method has the decided advantage over the other method that the samples can be tested under strictly comparable conditions which can be varied at will within wide limits. It is evident that in the balloon method, since the pressure of the atmosphere over the wool varies during the experiment, the relative humidity and consequently the regain of the wool will also vary. The cylinder method, being carried out at constant pressure, is

not subject to this drawback, and it has also been found to be more convenient. The experiments are more rapidly carried out and the calculations are somewhat simpler. The initial volume of the wool is also more reproducible.

The balloon method was so modified by Pidgeon and van Winsen (2), working in these laboratories, that experiments could be carried out under constant conditions of humidity, but this involved changes which further complicated the method.

Examination of Table VI, in which results are given for three different weights of wool, shows that the volume of the wool is proportional to the quantity of wool taken. Although the agreement with the smaller weight, 2.20 gm., is not very good at the lower pressures, it is good at the higher pressures, the agreement for the higher weight of 4.34 gm. is excellent for all pressures as compared to the 3.26 gm. sample. As the weights of the various samples taken for the tests varied only between 3.05 and 3.35 gm., the correction as made is justified.

Another correction which it was necessary to make before results could be compared was that due to the different moisture content of the wool at 50% and at 60% humidities. This difference amounted to about 1% of the weight of the wool. In order to compare the results obtained at 50% with those obtained at 60% humidity it was necessary to subtract 1% of the values obtained at 50% humidity, which is equivalent to comparing 3.25 gm. at 60% with 3.22 gm. at 50%.

The softest of the yarns tested as determined by feel was the No. 2 white yarn, followed by No. 2 dyed, while No. 1 dyed was the most harsh of the four. As indicated by the curves the results of the experiments place the yarns in the same order if the softness is associated with ease of compressibility.

The results also show that the area enclosed by the loop formed by the compression and release curves cannot be relied on to give a measure of the harshness. The areas of the four loops in Fig. 3 taken from top down are 119, 121, 127, 111 (in arbitrary units) while in Fig. 2 they are 150, 139, 140, 102. It is evident from these figures that the differences in areas for different samples are not large enough to enable one to use them as a measure of harshness. The experimental error for them also seems to be fairly large.

Examination of the curves shows that in order to compare the harshness or springiness of various wools it is not necessary to perform an entire cycle; it is sufficient to compare the volumes occupied by the wools under identical pressures or to determine under what pressures the wools will have the same volume. It is advisable to use a fairly high pressure as the agreement was always found to be better at the higher pressures but even though it may be better to carry out a full compression stroke, the release or return stroke is certainly not necessary. Attention must be drawn to the results of Winson which, if examined in this way, do not all agree with this view of harshness.

In the case of the super Shropshire wether and hog wools, the volume occupied by the hog wool is smaller than that of the wether wool for the same pressure; in other words it is more compressible and therefore would be softer. But this does not seem to hold in the case of some of the others, notably in the case of the mohair and veld wool where the mohair appears to be more compressible in spite of its greater springiness. It would be highly desirable then to carry out a large number of experiments with a wide variety of samples before deciding on the general applicability of the relation found in the case of the yarns tested.

The effect of humidity on the compressibility cannot be determined sufficiently well from the two series of experiments carried out at 50% and 60% humidity. Although in three of the samples the compressibility was higher at 50% this effect was reversed for the fourth sample which happened to be the harshest, as shown in Fig. 4. Tests at widely differing humidities will have to be made before a definite conclusion can be reached on this point. However the order of the curves for the four samples did not change from one condition to the other, so that for purposes of comparison it does not matter at what humidity the tests are made provided that the conditions are maintained constant during the tests. If Fig. 5, where the ratios of the volumes are plotted instead of the actual volumes, is examined instead of Fig. 4, the effect of humidity is the same on all four samples although the effect on the No. 2 undyed sample appears to be very small, while in Fig. 4 it was the greatest. It is doubtful then which of the two methods of plotting is the most valuable. Further tests would help to decide this point. The method of plotting the ratios to original volume suffers from the disadvantage that an error in determining this initial volume affects all the other points.

It might be questioned whether some of the differences noted in these samples are not due to dimensional attributes. This can hardly be so. The differences in the diameters and number of scales are not large and the difference in length seems to be the only possible cause of variation. But if the results of Winson are applicable here one would expect an opposite effect to that noted, namely that the No. 2 which has the longer fibres, would be the harsher (or less resilient as Winson terms it) of the two. It is probable that the greater length of the fibres in No. 2 did make it appear harsher but taking this into consideration would only increase the differences noted between the two wools. The supposition that was made in the introduction that the harshness was probably due to a greater resistance to compression seems therefore to have been borne out by the results of these experiments.

Schiefer has already proposed the use of resilience as a useful criterion of the "handle" or "feel" of fabrics when they are squeezed between the fingers, although he did not mention specifically harshness or softness.

Winson has used the term resilience to express the property being investigated. It is questionable whether the use of the term in this sense is justified. It would be better to reserve for it the meaning given in mechanics in which

it represents the amount of work which an elastic body is capable of doing in recovering from a stressed condition. Its general use to express the power of recovery of a material to its initial state would also be acceptable. However since the curves given all show the wool to come back to its original volume, applying this definition for resilience would show all the wools to be 100% resilient. The use of the term springiness instead of resilience would be more desirable. It is generally used to mean the capacity of resisting compression or deformation which is actually what is being measured in these experiments.

The use of the term resilience has been discussed by Pidgeon and van Winsen. Since the term is being used more and more in application to textiles it would be highly desirable that a suitable definition be proposed and accepted by all concerned.

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THE DECOMPOSITION OF ETHYL ALCOHOL OVER SOME POLY-COMPONENT CATALYSTS[1]

By E. H. Boomer[2] and H. E. Morris[3]

Abstract

Numerous experiments have been carried out on the decomposition of alcohol, alcohol and water, and alcohol and carbon dioxide mixtures over poly-component catalysts at temperatures up to 500° C. Quantitative data on the gaseous and the liquid products were obtained. The properties of the poly-component catalysts, as evidenced by the simple primary and secondary reactions, have been shown to be qualitatively those of the single components.

Methane can be produced in one or more of several secondary reactions, namely, the decomposition of acetaldehyde, the hydrogenation of carbon oxides and the decomposition of ethylene. Ethane can be produced in one or both of two reactions consisting of auto-oxidation and reduction of the alcohol, or the secondary hydrogenation of ethylene, confirming previous work. Carbon dioxide, in most cases, is formed as a result of the water-gas reaction and the decomposition of carbon monoxide. In other cases its origin is obscure. The results of certain experiments in which carbon dioxide and hydrogen were the major constituents of the off-gas cannot be explained in the same way. Reactions involving ketene decomposition and polymerization, and hydration of alcohol, have been suggested as possible explanations.

Introduction

In two previous papers (7, 8) from this laboratory the catalytic decomposition of ethyl alcohol was discussed, and it was suggested that the reactions occurring are numerous and complex. This paper is a further contribution dealing particularly with the origin of methane, ethane and carbon dioxide in such decompositions. In spite of numerous experimental results, the complexity of the reactions prevents more than a qualitative indication of the reactions involved. Many primary, and even more secondary, reactions are possible, the nature and course of which depend upon the catalyst, conditions of temperature, and space velocity used. Among the gaseous products may be hydrogen, carbon monoxide, carbon dioxide, ethylene, methane and ethane. The liberation of carbon is also possible and a few liquids such as water, aldehydes, esters and polymerization products can be formed. Little has been done in the present work with regard to the composition of the liquid products. Attention has been paid to the origin of methane because of the various possible reactions leading to its formation and to the formation of ethane and carbon dioxide, because of the relatively large amounts of these substances formed under certain conditions.

Literature Review

The formation of methane during the decomposition of ethyl alcohol may occur in several ways. The primary decomposition of alcohol to aldehyde,

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followed by the decomposition of aldehyde to methane and carbon monoxide, is probably the most frequent and largest source of methane. The hydrogenation of carbon monoxide may be mentioned as a second important source. While Razuvaev (40) finds only these two reactions and a third, the direct hydrogenation of ethyl alcohol under pressure, as sources of methane, the present authors believe that several other reactions must be considered in experiments at atmospheric pressure. The reactions that appear worthy of consideration, with relevant references, are as follows:

1. $CH_3CHO = CH_4 + CO$ (46)
2. $CO + 3H_2 = CH_4 + H_2O$ (3, 12, 13, 17, 42)
3. $2CO + 2H_2 = CH_4 + CO_2$ (3, 6, 12, 13, 17, 31)
4. $CO_2 + 4H_2 = CH_4 + 2H_2O$ (3, 17, 31, 51, 52)
5. $4CO + 2H_2O = CH_4 + 3CO_2$ (17, 33, 34)
6. $C + 2H_2 = CH_4$ (10, 11, 29, 36)
7. $n(C_2H_4) = CH_4 + C_3H_6 + C$, etc. (6, 10, 11, 14, 33, 34, 49, 50)

It is possible that any or all of these seven secondary reactions can be sources of methane. Some, such as 1 and 2, may be considered probable and even established by the elimination of others from the range of possibility.

There have been only two reactions proposed as sources of ethane that require consideration here. Engelder (15) suggested that ethane was formed by the hydrogenation of the primary product, ethylene, when hydrogen was present in the "nascent" state. Bischoff and Adkins (5) believe it more probable that auto-oxidation and reduction of ethyl alcohol give rise directly to ethane as follows:

8. $2C_2H_5OH = CH_3CHO + H_2O + C_2H_6$.

The authors concurred in this belief (7) at one time, but the present work suggests that both reactions occur in proportions that vary with experimental conditions.

The production of carbon dioxide during the decomposition of ethyl alcohol may occur through the operation of several reactions. The following secondary reactions may be listed as possibilities as shown by work done elsewhere:

9. $2CO = CO_2 + C$ (20, 48)
10. $C + 2H_2O = CO_2 + 2H_2$ (12, 13)
11. $CO + H_2O = CO_2 + H_2$ (52)

These are all common reactions to which a great deal of attention has been given, although only type references are made to each. In addition, Reactions 3 and 5 are considered as sources of carbon dioxide.

Sabatier and Mailhe (43) have shown that oxide catalysts may be reduced by alcohol vapor with the formation of carbon dioxide, but in the present work this reaction was impossible, or readily evident by its cessation upon complete reduction.

Brown and Reid (9) have suggested that the carbon dioxide is due to the condensation of acetaldehyde to an ester, which on decarboxylation yields carbon dioxide and a hydrocarbon. The decarboxylation of ethyl acetate has been reviewed by Sabatier (42) and further investigated by Adkins (1)

and found to proceed readily over certain catalysts. Armstrong and Hilditch (2) have reported the presence of ethyl acetate among the liquid products of the reaction of ethyl alcohol over nickel at temperatures above 350° C. As acetic acid has been reported so frequently as another product, it seems quite possible that the ester would be formed in many cases. If this is so, the decarboxylation mentioned above would form another possible source of carbon dioxide.

Lazier and Adkins (22) believe, however, that none of the above mechanisms are satisfactory and emphasize several factors that must be taken into consideration. These include the presence of carbon dioxide itself, the acidic nature of all condensates and the frequent observation of a brown water-insoluble resin. Lazier and Adkins developed a mechanism which will account for all these facts. They suggest that the catalyst employed is dehydrogenating, and a ketene is formed.

12. $CH_3CHO = H_2 + CH_2CO$.

The reaction between this ketene and more of the aldehyde would produce carbon dioxide and an unsaturated hydrocarbon, which would polymerize to produce the resin so often noted.

13. $CH_2CO + CH_3CHO = CO_2 + CH_2CHCH_3$.

The reaction between the ketene and water would produce acetic acid, while a reaction between this ketene and ethyl alcohol yields ethyl acetate. Incidentally they stated without comment that the presence of water in the reactants increased the percentage of carbon dioxide and hydrogen.

Experimental Method

The method of investigation has been described previously (7, 8) in sufficient detail except in one respect. Whereas the apparatus described was designed to handle liquids such as ethyl alcohol or aqueous solutions of ethyl alcohol, certain experiments reported now were carried out on carbon dioxide-ethyl alcohol mixtures. In these experiments the apparatus was modified to permit a controlled and measured supply of gaseous carbon dioxide to a saturator containing alcohol maintained at a definite temperature, the gas mixture from the saturator being conducted to the catalyst chamber.

Results and Discussion

Complete results will not be reported but only those necessary to illustrate the nature of the reaction as far as possible. Many data were obtained apart from those presented that confirmed the conclusions given and were of no interest otherwise. The addition of water or of carbon dioxide to the alcohol vapor entering the catalyst chamber was practised as a convenient method of reducing the space velocity. It has been shown by Gilfillan (16) and also in this laboratory that carbon dioxide has little or no effect on the course of the reactions. Similarly, several reports (2, 19, 22, 41) have shown that water acts largely as an inert diluent, but may exert a repressing effect on the reaction.

The Formation of Methane

As has been indicated in the results of other workers, nickel promoted the aldehydic decomposition of ethyl alcohol; the aldehyde was decomposed to methane and carbon monoxide and the latter further broken down to free carbon and carbon dioxide. The results given in Table I indicate these reactions quite clearly. The catalyst, No. 12, was prepared by the ignition of nickel nitrate on asbestos. A second catalyst, nickel chromate, behaved similarly.

TABLE I

EQUIMOLAR ALCOHOL AND WATER.

Catalyst No. 12. Nickel on asbestos by ignition

Temp., °C.	Composition of gaseous products, % by vol.						
	CO_2	CO	Total, as CO	CH_4	H_2	C_2H_6	C_2H_4
330	0.8	25.7	27.3	28.6	40.9	4.0	Nil
375	19.5	5.5	44.5	42.5	30.0	2.5	Nil
400	21.8	3.4	47.0	50.0	24.7	Nil	Nil
450	23.4	4.4	51.0	48.6	23.6	Nil	Nil
500	20.6	2.0	43.2	45.2	32.2	Nil	Nil

The occurrence of ethane in a reaction such as this has been discussed in an earlier paper (8). It is quite evident from the balances obtained in these experiments that the methane is obtained directly from the decomposition of the aldehyde. The hydrogenation of carbon monoxide or carbon dioxide is inappreciable.

The hydrogenation reaction takes place in the presence of carbon dioxide and catalyst No. 22. This catalyst was prepared by mixing together 4 moles of chromic oxide, 1 mole of zinc oxide, 0.5 mole of alumina and traces of copper powder and sodium carbonate. These were well mixed, ground to a paste, and dried to a very hard catalyst which was treated with hydrogen at 300–350° C. Catalyst No. 24 contained 1 mole of zinc oxide, 1 mole of chromic oxide, 0.5 mole of cupric oxide and a trace of copper powder to promote reduction (33, 34). This catalyst was similarly treated. Catalyst No. 27 was prepared by precipitating together in slightly alkaline solution an equimolar mixture of potassium chromate, nickel

TABLE II

EQUIMOLAR ALCOHOL AND WATER

Catalyst No.	Temp., °C.	Composition of gaseous products, % by vol.				
		CO_2	H_2	CH_4	CO	C_2H_4
22	400	10.0	85.5	2.3	Nil	2.1
	500	14.4	78.0	2.3	Nil	5.3
24	400	9.5	86.2	1.6	Nil	2.7
	500	10.4	84.2	1.6	Nil	3.8
27	350	7.3	91.2	Nil	Nil	1.5
	450	18.8	77.8	Nil	Nil	3.4

nitrate, and ferric nitrate, giving an orange yellow precipitate. The liquid was decanted, and the filtrate washed, dried at 110° C., crushed and reduced as before. The results with these three catalysts are given in Table II, with those obtained with catalyst No. 27 for purposes of comparison. The liquid products were characterized by the occurrence of a high boiling oily fraction.

The fact that these catalysts were all essentially dehydrogenating suggested the production of considerable quantities of aldehyde; the total amount of methane was relatively low and if some of the aldehyde was decomposed, the carbon monoxide was either hydrogenated to methane or decomposed to carbon dioxide and carbon. The latter step is rendered improbable by the fact that very little carbon was observed on the catalyst. The excess of water present would decrease the tendency to hydrogenate carbon monoxide (17). It seems improbable therefore that the aldehyde was decomposed. The decomposition of ethylene, as previously shown, gives carbon and ethane as well as methane and hydrogen. The absence of carbon renders the ethylene an unlikely source of the methane. It should also be noted that the methane would increase as the ethylene increased, if there was any decomposition, and such is not the case. The most reasonable mechanism then, involves the hydrogenation of carbon dioxide, since this reaction is not suppressed by water and both gases are present in large proportions. The relatively large amounts of carbon dioxide occurring concurrently with oily condensates will be discussed later. The results with catalyst No. 27 seem to verify the above conclusions; the aldehyde formed was obviously not decomposed, nor was the ethylene polymerized. This catalyst, however, did not promote the hydrogenation of carbon dioxide with the consequent formation of methane, although a hydrogenating reaction might have been expected.

Catalyst No. 28A was also interesting in its results. It was prepared by depositing copper and chromium on silica gel as previously reported (7) and the results have been given. The methane produced over this catalyst could arise from two sources; the decomposition of aldehyde as in Reaction 1, and the hydrogenation of carbon dioxide as in Reaction 4. It is recognized that the decomposition of ethylene would also lead to an analytical excess of water among the products, but the ratio of ethane to methane is not high enough to allow this as a possible source of methane in the light of the work of other investigators.

Another catalyst, No. 28B, which also deserves mention, was that prepared as above, using nickel in addition to copper and chromium on silica, and prepared in a similar manner. The results are given in Table III. These results seem to offer two sources of methane at 400 and 450° C., the hydrogenation of carbon dioxide and the decomposition of ethylene (Reactions 4 and 7).

TABLE III

EQUIMOLAR ALCOHOL AND WATER.
Catalyst No. 28B—nickel, copper and chromium on silica

Temp., °C.	Composition of gaseous products, % by vol.				
	CO_2	C_2H_4	H_2	CH_4	CO
350	1.1	56.8	42.1	Nil	Nil
400	3.4	57.8	35.0	3.8	Nil
450	9.3	45.0	36.2	8.4	1.1

The action of the nickel in this catalyst is quite evident, but in view of other results (8) in which nickel was found to be more active than either chromium or copper, it was expected that the hydrogen content of the gases would increase instead of decrease. The solution of this anomaly is offered by the hydrogenation of carbon dioxide which requires four volumes of hydrogen for each volume of methane produced. As the temperature was increased from 350 to 400° C., the ethylene content also increased as would be expected from the above, but at 450° C. there was a surprising decrease, and at the same time the carbon dioxide and methane increased. This seems to suggest that some of the ethylene produced was decomposed, including methane as the main product of the reaction with an inexplicable absence of ethane. The decomposition of the aldehyde was evidently not of large magnitude.

TABLE IV

CARBON DIOXIDE AND ALCOHOL.

Catalyst No. 33A—nickel and zinc oxides

Temp., °C.	CO_2 Total	CO_2 Produced	C_2H_4	H_2	CH_4	CO
350	45.2	10.7	Nil	5.9	45.7	3.2
400	47.8	10.8	Nil	10.4	38.1	3.7
450	56.0	18.2	Nil	11.5	28.9	3.6

Catalyst No. 33A, prepared by the precipitation of nickel and zinc hydroxides from an equimolar solution of their nitrates with sodium hydroxide, followed by thorough washing, was studied using carbon dioxide with the alcohol. The results of these experiments are given in Table IV, in which the second column includes carbon dioxide added to the reactants as calculated from the relative gas volumes.

With this catalyst, the formation of the methane was apparently due to the decomposition of aldehyde and the hydrogenation of the carbon oxides. The large excess of carbon dioxide in the gases appeared to favor the formation of methane. The decrease in the percentage of methane was probably due to a decrease in the activity of the catalyst for this hydrogenation reaction, and may be only relative owing to the fact that more of the aldehyde was decomposed, involving the ultimate formation of carbon dioxide as evi-

TABLE V

EQUIMOLAR ALCOHOL AND WATER.

Nickel–chromium oxide catalysts

Catalyst	Temp., °C.	Composition of gaseous products, % by vol.				
		CO_2	H_2	C_2H_4	CH_4	CO
52 80% Ni	240	8.3	40.8	1.4	30.2	19.5
	300	16.4	39.4	0.5	32.4	11.3
	350	22.0	31.8	0.5	40.9	4.7
	400	21.6	32.2	0.5	40.0	4.8
	450	20.4	40.4	0.4	32.1	6.8
	500	16.0	49.3	0.4	23.9	10.4
56 97% Ni	235	16.6	39.0	0.7	33.9	9.9
	265	23.5	25.4	0.8	48.1	2.3
	300	24.4	17.8	0.4	57.0	0.6
	325	24.3	29.0	0.6	43.8	2.4
	350	23.1	30.9	0.6	43.1	2.2

denced by the much higher percentage of this compound at 450° C. Such results are in accord with those to be discussed on the formation of carbon dioxide.

A series of catalysts were prepared from nickel and chromium and the results obtained with two of these are presented in Table V. These data have been taken from a previous paper (8).

The results with the catalysts shown in Table V are very interesting. It will be noticed that at a certain temperature, varying with the catalyst, the carbon dioxide and methane reached a maximum, while the carbon monoxide and hydrogen reached a minimum. It seems from this that the extent of decomposition of carbon monoxide varies with the temperature in a regular manner. Consequently the percentage of carbon dioxide formed varies in the same manner, and an increase in the amount of carbon dioxide accelerates the hydrogenation reaction, involving decreases in the hydrogen content and an increase in the amount of methane. With this series of catalysts this type of reaction was observed to be the usual one. Most catalysts did not behave in so clear-cut a manner, however, as shown by the products obtained when the catalysts of Audibert and Raineau (4) were used. These catalysts contained, in the case of No. 44, iron, copper, manganese, phosphorus and potassium, while No. 45 contained iron, copper, manganese, boron and potassium. The results are given in Table VI. With results such as these the source of the methane is rather difficult to determine with any degree of certainty. No carbon was deposited on the catalyst.

TABLE VI

EQUIMOLAR ALCOHOL AND WATER.
Audibert and Raineau catalysts

Catalyst	Temp., °C.	Composition of gaseous products, % by vol.				
		CO_2	H_2	CH_4	C_2H_4	CO
44	350	6.9	89.3	0.7	3.1	Nil
	400	18.5	78.3	Nil	3.2	Nil
45	350	7.3	83.6	8.0	1.2	Nil
	400	18.2	77.9	1.5	2.5	Nil

The Formation of Ethane

A large number of catalysts have been investigated in this research, and some of the results have been discussed in another paper (7). It might be expected that a lower space velocity would increase the possibility of hydrogenation of ethylene when a catalyst that possesses the properties necessary to promote this reaction is used. Actually the results have indicated that this is the case with certain catalysts which cause ethane formation in the pyrolysis of carbon dioxide and alcohol mixtures but not in the pyrolysis of alcohol and water. The space velocity of the alcohol was much less when carbon dioxide was added. This, however, does not preclude the possibility of the hydrogenation reaction occurring at higher space velocities.

On the other hand, where the source of the ethane is the primary reaction of Bischoff and Adkins, it might be expected that the presence of diluents

such as carbon dioxide or water would serve merely to reduce the proportional quantity of ethane formed in the first case; or reduce the catalytic area available for alcohol decomposition, with the subsequent reduction of ethane production in the second case. These effects have been identified quite definitely with some catalysts.

Indications have also been obtained of the heat sensitivity of both of these reactions as shown by the change in activity of the catalyst with various treatments, such as oxidation and reduction between experiments. These conclusions are clearly illustrated in the results.

A variety of catalysts have been used and their preparation will be briefly described, except those already given. The numbers refer to the series used in this laboratory and are retained in this form for convenience in further references.

Catalyst No. 16—An equimolar mixture of zinc oxide and chromic oxide triturated in water and dried at 110° C.

Catalyst No. 28C—Similar to 28A but containing nickel as well as copper and chromium.

Catalyst No. 30—Ten moles of magnesium and one mole of chromium precipitated together, using ammonium hydroxide and a solution of the nitrates.

Catalyst No. 31B—One mole of cupric hydroxide from cupric chloride by precipitation with sodium hydroxide, with the addition of one-tenth mole of manganese dioxide as a promoter.

Catalyst No. 31F—As with 31B but using $\frac{1}{10}$ mole of each of titanic and molybdic acids as promoters.

Catalyst No. 33C—75% of nickel and 25% of zinc as hydroxides, by precipitation from a nitrate solution with sodium hydroxide.

Catalyst No. 36A—One mole of precipitated chromic hydroxide containing $\frac{1}{10}$ mole of titanic acid.

Catalyst No. 36B—As 36A, with lead oxide as the promoter.

Catalyst No. 36C—As 36A, with molybdic acid as the promoter.

Catalyst No. 41—Five moles of zinc oxide and one mole of molybdic oxide suspended in water. The suspension was evaporated to dryness with constant stirring using a motor stirrer.

The results given in Table VII are those obtained with carbon dioxide and alcohol. The column "Space velocity" refers to the rate of flow of carbon dioxide in cc. per min.; with those having a value of 25 cc. per min. the rate of alcohol flow was about 0.04 cc. per min. Table VIII contains results of experiments in which alcohol and water were used with rates of flow that varied slightly, as indicated. A comparison of results obtained with certain catalysts when carbon dioxide and water were used as the diluents, with the consequent variation in space velocity, is shown in Table IX. The results with catalyst No. 33C, and using carbon dioxide or water and alcohol and absolute alcohol, are given in Table X where a ready comparison is possible.

TABLE VII

RESULTS OBTAINED WITH CARBON DIOXIDE AND ALCOHOL

Catalyst No.	Temp., °C.	Composition of gaseous products, % by vol.			Space velocity
		C_2H_4	H_2	C_2H_6	
16	450	2.5	35.6	4.3	50
	450	2.9	35.3	2.7	25
24	350	0.6	14.6	5.5	50
	450	1.8	36.5	9.1	30
	450	2.6	33.3	2.3	50
30	350	0.2	2.3	3.0	25
	450	1.6	27.4	8.7	25
31B	450	1.0	36.1	8.6	25
	450	0.4	11.0	2.4	100
31F	450	0.6	25.6	7.7	25
33C	450	Nil	17.9	10.7	25
	350	Nil	12.6	Nil	25
		Oxidized and reduced			
	300	Nil	29.0	6.3	25
	275	Nil	27.8	Nil	25
41	350	3.1	16.1	5.5	30

An examination of the results in Table VII points quite definitely to hydrogenation of ethylene as the source of ethane in every case except Catalyst No. 33C. With catalysts Nos. 24 and 30 the temperature effect is quite evident, the total reaction not being as great at 350° C. In consequence of the reactants available for hydrogenation being diminished, the ethane content is correspondingly lower. Catalysts Nos. 24 and 31B illustrate the influence of space velocity; the higher the velocity the lower the ethane content as might be expected from the decreased time the reactants are in contact with the catalyst. In the case of catalyst No. 33C it does not seem probable that any ethylene produced would be completely hydrogenated but indicates rather

TABLE VIII

RESULTS OBTAINED WITH WATER AND ALCOHOL

Catalyst No.	Temp., °C.	Composition of gaseous products, % by vol.						Rate of flow, cc./min.
		CO_2	C_2H_4	H_2	CO	CH_4	C_2H_6	
28B	450	10.3	21.9	61.0	0.6	5.3	0.9	0.20
28C	350	1.1	56.8	42.1	Nil	Nil	Nil	0.27
	400	3.4	57.7	35.1	Nil	3.8	Nil	0.25
	450	9.2	45.0	36.2	1.1	8.5	Nil	0.31
33C	300	3.0	0.4	65.0	10.0	15.0	6.6	0.35
	500	20.4	Nil	44.6	6.8	22.3	5.9	0.33
		Oxidized and reduced						
	275	2.5	0.2	56.5	15.3	23.6	1.9	0.37
36A	450	2.3	38.5	49.7	Nil	3.0	6.5	0.55
36B	450	9.7	17.9	8.2	0.2	Nil	64.0	0.53
36C	450	5.8	21.0	69.0	Nil	Nil	4.2	0.60

TABLE IX

COMPARISON OF RESULTS OBTAINED WITH WATER AND CARBON DIOXIDE

Catalyst No.	Temp., °C.	Alcohol with	Composition of gaseous products, % by vol.			Rate of flow, cc./min.
			C_2H_4	H_2	C_2H_6	
24	450	H_2O	3.5	89.2	Nil	0.21
	500		3.5	86.2	Nil	0.21
	350	CO_2	0.6	14.6	5.5	0.08
	450		2.6	33.3	2.3	0.08
	450		1.8	36.5	9.1	0.08
30	450	Alone	14.0	80.9	Nil	0.55
	500		12.7	71.3	Nil	0.55
	350	CO_2	0.2	2.3	3.0	0.04
	450		1.6	27.4	8.7	0.04
41	350	H_2O	12.7	56.3	Nil	0.40
	450		10.8	69.5	Nil	0.63
	350	CO_2	3.1	16.1	5.5	0.04

TABLE X

COMPARISON OF RESULTS OBTAINED WITH CATALYST No. 33C

Alcohol with	Temp., °C.	Composition of gaseous products, % by vol.			Rate of flow, cc./min.
		C_2H_4	H_2	C_2H_6	
CO_2	350	Nil	12.6	Nil	0.04
	450	Nil	17.9	10.7	0.04
	Oxidized and reduced				
	275	Nil	27.8	Nil	0.05
	300	Nil	29.0	6.3	0.05
H_2O	300	0.4	65.0	6.7	0.35
	500	Nil	44.6	5.9	0.33
	Oxidized and reduced				
	275	0.2	56.5	1.9	0.37
Alone	300	1.2	59.8	11.2	0.23
	Oxidized and reduced				
	375	3.2	50.7	13.6	0.24
	450	3.4	53.0	17.1	0.31

that ethylene was not produced. This assumption seems justified as will be shown later. The temperature effect is quite evident with this catalyst and the variation in activity with vigorous treatment is also shown by the change in reaction following oxidation and reduction. This action of the catalyst is more evident in Table X.

The experimental results shown in Table VIII are more variant in nature. Catalyst No. 28A has been reported previously (7) and from a consideration of the results with catalyst No. 28B it would seem that the only effect of the addition of alkali to the catalyst was to reduce its activity and possibly promote polymerization of ethylene. If the ethane produced with these silica catalysts had come from the hydrogenation of ethylene, it was anticipated that the addition of nickel would increase this hydrogenation reaction. However as shown by the results with catalyst No. 28C there was no ethane

formed. The primary reaction was apparently inhibited by the presence of nickel in the catalyst and no indication of hydrogenation was evident. This result confirms the primary mechanism as the source of ethane with catalysts Nos. 28A and 28B. The results with catalyst No. 33C will be discussed later but the small ethylene content renders the hydrogenation reaction improbable in view of the results obtained with carbon dioxide and alcohol.

The dehydrating action of chromium is well known and the results obtained with catalyst No. 36 were therefore not unexpected. From the results shown in Table VII with catalyst No. 31F containing titanium and molybdenum it may be said that these metals behave similarly to chromium, promoting hydrogenation of ethylene. This action is quite evident with catalysts Nos. 36A and 36C. The catalytic activity of lead oxide has not been thoroughly examined, but Madenwald, Henke and Brown (27) found that it was very active in the hydrogenation of nitrobenzene and consequently the high percentage of ethane with catalyst No. 36B can be readily accounted for on the basis of this activity. In these chromium catalysts the source of ethane is quite evidently hydrogenation of ethylene.

In Table IX the results obtained with three catalysts, using carbon dioxide and alcohol, and water and alcohol, are compared. The conclusions which may be drawn are quite evident. In each case the decreased rate of alcohol flow using carbon dioxide is accompanied by ethane formation, due undoubtedly to hydrogenation of ethylene.

The primary formation of ethane with catalyst No. 33C is clearly shown in Table X. As already mentioned the presence of diluents serves only to decrease the volume of alcohol decomposed and decrease the space velocity. With carbon dioxide and alcohol the actual percentage of ethane produced in the decomposition is much greater than that indicated by the gas analysis, owing to the presence of excess carbon dioxide as carrier. In the case of diluted alcohol the presence of water reduces the amount of alcohol which will come in contact with the catalyst, and the extent of reaction is decreased. Using absolute alcohol, however, both of these effects are overcome, and this is clearly shown in the values obtained for ethane.

The Formation of Carbon Dioxide

The results to be presented are not entirely in agreement with the mechanisms already discussed. Several experiments showed the production of carbon dioxide under conditions that preclude the decomposition of carbon monoxide. The results of these experiments were of two types: (i) in some cases a gas, largely carbon dioxide and hydrogen, and oily condensates were obtained; (ii) in others, a gas was obtained as in (i), but there was no oily condensate. The mechanisms proposed by Lazier and Adkins and by Brown and Reid, previously described, might account for the first of these classes. An objection lies in the small yields of higher hydrocarbons found and the absence of propane. As a result, and to cover the second class, a new mechanism is proposed. It is not necessarily exclusive but rather is supplementary

to the mechanism of Lazier and Adkins. Confirmation of the possibility of the ketene reaction has been obtained and a hydrocarbon oil of the empirical formula of ethylene, but of high molecular weight, has been obtained. In addition oils were obtained repeatedly of the empirical formula C_5H_8O, approximately. The boiling point and molecular weight were high.

Table XI shows the results obtained with catalyst No. 33B and should be considered together with Table I. Catalyst No. 33B was made by precipitating zinc and nickel oxides from an equimolar solution of the nitrates, washing the precipitate, drying at 110° C., and reducing with hydrogen at 300° C. It is quite evident from the data that the origin of the carbon dioxide can be explained simply as due to the decomposition of carbon monoxide produced from acetaldehyde formed in the primary reaction. The parallelism between total oxides of carbon and methane is definite evidence.

TABLE XI

EQUIMOLAR ALCOHOL AND WATER OVER CATALYST No. 33B

Temp., °C.	Composition of gaseous products, % by vol.			
	CO_2	CO	CH_4	Total oxides of carbon, as CO
275	1.8	4.4	11.5	8.0
325	2.7	5.3	10.7	10.7
450	4.0	4.6	13.0	12.6

The copper-chromium-silica catalyst previously discussed (5) produced very little carbon monoxide and no free carbon, but did yield a considerable amount of carbon dioxide.

Very little oil was produced and evidently other reactions yielding carbon dioxide were taking place to a considerable extent. The behavior of this catalyst and those of a similar nature will be referred to later.

As already mentioned, two types of oils have been identified; one a pure hydrocarbon and the other an oxygenated compound. As a catalyst capable of producing the former substance No. 30 was typical. On passing a mixture of carbon dioxide and alcohol vapor over this catalyst, a small amount of oil was obtained which showed on combustion analysis, 13% of hydrogen and 85.9% of carbon, corresponding approximately to an empirical formula of C_2H_4. It had a high molecular weight and a high boiling point. Such a substance might be formed from a ketene according to Adkins or by the polymerization of ethylene; the low percentage of ethylene in the gas coupled with the fact that alumina is primarily dehydrating (42) renders the latter reaction probable. Decarboxylation of an ester does not appear as reasonable.

The oxygenated compound has been identified in several cases using alcohol and water mixtures, and examples of the gas analyses obtained from reactions of this nature are given in Table XII. The results with catalyst No. 30, given in Table IX and repeated here for two temperatures, were obtained with absolute alcohol.

In all of these cases the oil closely approximated a composition corresponding to the formula C_5H_8O, and appeared to be a polymer of high molecular weight. The oil obtained with catalyst No. 30 was tested by the cryoscopic method for its molecular weight using benzene as the solvent, and a value of 240 was obtained, which probably corresponds to a trimer. The analyses of the off-gases show relatively low amounts of carbon monoxide and methane, which indicates slight secondary decomposition of acetaldehyde. The large hydrogen content, on the other hand, indicates considerable dehydrogenation, and these facts seem to conform with a mechanism to be suggested, in which much of the aldehyde is assumed to undergo further reaction. The water formed in the dehydration of the alcohol, or originally present in the mixture, might have reacted to produce carbon dioxide, but the absence of other products of these reactions reduces such a possibility.

TABLE XII

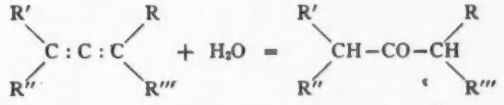
EXPERIMENTS GIVING CARBON DIOXIDE AND HYDROGEN AND OIL

Catalyst No.	Temp., °C.	Composition of gaseous products, % by vol.				
		CO_2	C_2H_4	H_2	CO	CH_4
22	400	9.2	2.3	88.6	Nil	Nil
	450	8.7	4.9	85.5	Nil	1.0
	500	14.7	3.8	77.8	Nil	3.6
24	450	8.3	3.5	89.2	Nil	Nil
	500	10.6	3.5	86.0	Nil	Nil
27	350	7.3	1.6	91.0	Nil	Nil
	400	18.5	2.8	78.5	Nil	Nil
	450	18.9	3.1	76.8	0.7	0.7
	500	18.9	4.3	76.7	Nil	Nil
30	450	4.8	14.0	80.9	Nil	Nil
	500	10.4	12.7	71.3	2.6	2.9

The following mechanism is offered to account for these oils. This mechanism involves preliminary decomposition of the ketene with the formation of allene and carbon dioxide.

14. $2H_2CCO = CO_2 + H_2CCCH_2$.

Allene readily undergoes various reactions owing to its chemical activity. Lebedev (23) has reported the ease with which it is polymerized, forming compounds from the dimer to the hexamer. He also noted that the trimer was readily oxidized. Meinert and Hurd (30) also found polymerization of allene at 400–600° C. to proceed relatively easily. He obtained 90% conversion to the liquid dimer and trimer at 500° C. Allene hydrocarbons readily add on water in the presence of catalysts to form ketones (42).

15. 

In this case acetone would be formed, and Adkins (42) states that in the presence of certain catalysts acetone will condense.

However, an addition reaction between allene and acetaldehyde would yield directly a compound with the composition C_5H_8O. The exact chemical

nature of such a product is difficult to predict, but there are several compounds, such as ethylidene acetone or tiglic aldehyde, which could be formed by a condensation reaction. The compound, C_6H_8O, being unsaturated, would be likely to condense to a polymeric form. Such a polymer might possess the properties shown by the substance found, and apparently the experimental conditions favor its formation. The slight variations in the molecular percentages shown on combustion analyses may be explained by the presence of small amounts of other substances which are possible products of the reaction. Owing to the relatively small quantities of product obtainable, complete separation and identification are very difficult. The reaction previously outlined for the original ketene decomposition involving acid formation will still be possible. It is interesting to note that Losanitsch (26) found that the exposure of ethylene and carbon monoxide mixtures to a silent electric discharge resulted in the formation of a dark brown liquid. The liquid had the formula C_6H_8O and appeared to be a dimer. Such or similar reactions cannot be ruled out in the present case.

The chief objection to the mechanism proposed lies in Reaction 14. There is no evidence for this reaction and it has been shown (35) that ketene decomposes to carbon monoxide and ethylene. This is true for temperatures in excess of 1000° C. over platinum and does not rule out entirely the reaction proposed.

A third type of result is given in Table XIII using equimolar alcohol and water and the catalysts described below. The gas produced was essentially carbon dioxide and hydrogen, and the liquids contained no high boiling fractions at all. Carbon was not deposited in appreciable amounts on the catalysts. The catalysts were prepared as follows: No. 37 was normal zinc chromate, precipitated from zinc nitrate with potassium chromate. Catalyst No. 43 contained five moles of zinc hydroxide and one mole of chromic hydroxide precipitated from the nitrates with potassium hydroxide, and washed thoroughly. Catalysts Nos. 44 and 45, the same as used previously, were prepared by the method of Audibert and Raineau (4) and contained copper, manganese, iron, potassium and phosphorus or boron.

TABLE XIII

EXPERIMENTS GIVING CARBON DIOXIDE AND HYDROGEN WITH NO OIL

Catalyst No.	Temp., °C.	Composition of gaseous products, % by vol.				
		CO_2	C_2H_4	H_2	CO	CH_4
37	350	5.6	6.7	76.3	3.3	8.1
	450	17.3	2.4	77.7	1.3	1.1
43	350	5.3	4.0	88.6	Nil	2.1
	450	12.9	6.4	79.6	Nil	1.1
44	350	7.3	1.4	83.3	Nil	8.0
	450	18.1	2.5	77.7	Nil	1.6
45	350	6.8	3.0	88.1	0.2	1.9
	450	18.4	3.0	78.6	Nil	Nil

At first sight, reaction No. 3 or 5 or both together with dehydrogenation of alcohol to aldehyde might appear to account essenti-

ally for these results. It is necessary only to assume some slight dehydration also to account for the ethylene. This may be true at 350° C., but is not adequate to explain the results at 450° C. The absence of carbon formation, the equilibrium conditions of reaction No. 3 or 5 and the small amounts of methane and carbon monoxide, compared to the production of carbon dioxide, taken together make it necessary to seek some other mechanism. No satisfactory mechanism can be proposed at present but the following may be suggested.

16. $C_2H_5OH + H_2O = 2CH_3OH$
17. $CH_3OH + H_2O = CO_2 + 3H_2$.

Three difficulties are at once apparent. The first reaction, 16, has not been shown to occur, although the isomer of ethyl alcohol, methyl ether, will behave in such a manner. Second, methyl alcohol was not found among the products of the reaction and its presence might be expected in small amounts at least. Lastly and most important, it is probable from work done here and elsewhere that the second reaction, 17, occurs in two stages; the decomposition of methanol to carbon monoxide and hydrogen followed by the water-gas reaction giving carbon dioxide. The small amounts of carbon monoxide surviving make the reaction extremely doubtful.

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NON-BASIC CONSTITUENTS OF THE LEAVES AND ROOTS OF *ADLUMIA FUNGOSA*, GREENE[1]

By Léo Marion[2]

Abstract

An investigation of the water-insoluble constituents of this plant has disclosed the presence of an unidentified substance, $C_{28}H_{56}O_2$(?), of adlumiasterol which forms a monoacetate, of a phenolic substance occurring with a mixture of fatty acids, and a red pigment, m.p. 286° C. Fumaric acid and a sterolin also occur together with 3 : 4–methylenedioxyphthalide which is obtainable as well by hydrolysis of adlumine.

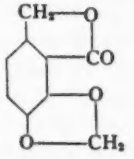
Small quantities of the four alkaloids protopine, adlumine, adlumidine and bicuculline were also present.

The present investigation is incidental to that carried out by Manske on the alkaloids of *Adlumia fungosa*, Greene (1). In the course of his work on this plant Manske obtained a methanolic extract E, which could be separated into a fraction S, soluble in dilute acid, and a residue R, insoluble in that medium. It is the study of that residue which is now reported.

Previous investigators of this plant have largely restricted their attention to its alkaloids and attached little or no importance to the non-basic constituents (4, 5). Besides the four bases, protopine, adlumine, adlumidine and bicuculline, small quantities of which were still present in the water-insoluble fraction, the latter contained a substance, $C_{28}H_{56}O_2$, m.p. 82° C., which suffers no depression in melting point when admixed with cerotic acid, but does not possess the properties of either an acid or an ester. When treated with various reagents it fails to produce the usual derivatives of an alcohol. A sterol, $C_{39}H_{68}O_2$, is also present in the water-insoluble fraction; it belongs to the type $C_nH_{2n-10}O_2$, examples of which are on record (3). As in the cases already known it gives rise to a monoacetate only. For convenience it may be designated adlumiasterol, from the generic name of the plant. In the accumulated mother liquors of adlumiasterol a red pigment, m.p. 286° C., was found to occur in very small quantity.

The fat, separated with the aid of petroleum ether, yielded a mixture of fatty acids and a substance, insoluble in sodium bicarbonate but soluble in sodium hydroxide, which possesses phenolic properties and melts at 115° C.

A large quantity of fumaric acid had already been isolated from the water-soluble extract and a small amount of the same acid was found present in the insoluble residue, together with a substance identified as 3:4–methylenedioxyphthalide (I) derivable from adlumine. Whether 3:4–methylenedioxyphthalide occurs as such in the plant cannot be definitely stated, since its production by hydrolysis of adlumine in the course of the process of isolation of the alkaloids appears equally possible.



(I)

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The extract also contained an appreciable quantity of a sterolin, $C_{33}H_{56}O_6$, which was characterized by the preparation of its acetate and benzoate; on hydrolysis, it produced a sterol and glucose. In this connection it is noteworthy that the sterol obtained on hydrolysis of the sterolin is different from that which occurs in the free condition in the plant.

Experimental

The dried and ground material (11 kilos) when thoroughly extracted with methanol yielded a solution (extract E) which was separated into an acid-soluble fraction S and an insoluble residue R (1). Besides containing much chlorophyll, the residue was very soft and oily; in order to facilitate its extraction in a Soxhlet apparatus, it was found expedient to mix it with shredded asbestos. This was done with the aid of alcohol which was subsequently evaporated. The hard cake thus produced was broken up and extracted successively with petroleum ether, ether, chloroform, ethyl acetate and methanol.

Petroleum Ether Extract

Following the removal of the solvent by distillation the residual oil was saponified with alcoholic potash and separated into acidic and unsaponifiable fractions.

Isolation of a Substance, $C_{28}H_{56}O_2$(?)

A solution of the unsaponifiable matter in hot acetone deposited, on cooling, copious shining flakes of a substance (9.3 gm.) which, after several recrystallizations from boiling acetone, melted at 81–82° C. When distilled under diminished pressure (255–256°/1.5 mm.) and recrystallized again from boiling acetone, this substance melts at 82–83° C. Calcd. for $C_{28}H_{56}O_2$: C, 79.24; H, 13.21%; M.W. 424. Found: C, 79.41, 79.54; H, 13.78, 13.72%; M.W. 413, 404 (Rast). It could not be saponified, and an attempt to esterify it by boiling with methanolic sulphuric acid likewise yielded the unchanged substance. Treatment with acetic anhydride, *p*-nitrobenzoyl chloride and phenylisocyanate failed to produce derivatives. Owing to the facts that the composition of the substance is very close to that of cerotic acid, that it has the same melting point and that admixture with an authentic specimen did not depress the melting point, the following experiment was carried out to prove, or disprove, the possible identity. A solution of a known weight of the substance in hot alcohol was titrated in the presence of phenolphthalein against standardized base. It did not neutralize any base whereas cerotic acid under the same conditions can be titrated readily. An attempt to oxidize the substance with a solution of chromic acid in glacial acetic acid produced an acid which, recrystallized from methanol, melted at 59° C. Although the substance appears to be an alcohol, its abnormal behavior is such as to make its identity extremely uncertain.

Isolation of Adlumiasterol, $C_{29}H_{48}O_2$

The acetone solution from which the aliphatic alcohol had crystallized was distilled and the crystalline residue dissolved in boiling methanol.

Repeated separation from boiling methanol finally yielded the sterol as lustrous flakes melting at 151–152° C. Calcd. for $C_{39}H_{68}O_2$: C, 82.39; H, 11.98%. Found: C, 82.72, 82.47; H, 11.74, 11.83%. The acetate, prepared by boiling with acetic anhydride in the presence of pyridine, melts at 136–137° C. Calcd. for $C_{41}H_{70}O_3$: C, 80.6; H, 11.48%. Found: C, 81.93; H, 11.16%. Adlumiasterol, as this substance might be named, therefore, belongs to a class of the general formula, $C_nH_{2n-10}O_2$, the known examples of which, however, are not identical with it.

The accumulated mother liquors from the recrystallizations of adlumiasterol exhibited a deep red coloration and, on concentration, yielded a dark red oil. The oil was dissolved in a little hot methanol (charcoal) and the solution allowed to evaporate spontaneously. After prolonged standing the residue crystallized into a mixture of flakes and slender prisms of a beautiful deep red color. The latter were separated mechanically, freed of adhering sterol by rapid washing with warm methanol and dried, m.p. 286° C. The quantity of crystalline pigment which could be freed of sterol and isolated in an uncontaminated condition was, unfortunately, too small for analysis.

Isolation of a Phenolic Substance

The ethereal solution of the liberated acids obtained from the saponified fat was extracted with a 5% aqueous solution of sodium bicarbonate which removed the fatty acids, and with a 5% aqueous solution of sodium hydroxide. A stream of carbon dioxide was passed through the latter extract and the precipitated substance was collected in ether and recrystallized several times from a mixture of ethyl acetate and methanol. It separated from this solvent as small, white crystals melting at 115° C. Calcd. for $C_8H_{16}O$: C, 75.0; H, 12.49%. Found: C, 75.04, 75.45; H, 12.33, 12.44%. The quantity isolated was too small to permit further identification. The fatty acids were not further investigated.

Ether Extract

The residue obtained on distillation of the ether consisted of a dark green, resinous mass mixed with a white, crystalline material. It was digested with one litre of ether and filtered in order to separate the white material which was less soluble than the rest.

Isolation of Fumaric Acid

The ethereal solution was shaken with 5% aqueous solutions of ammonium carbonate, potassium carbonate and sodium hydroxide, and each of these solutions was acidified and extracted with ether. In the course of the extraction with potassium carbonate, a crystalline substance separated out at the interface; it was collected and treated as described further on. From the ammonium carbonate solution was obtained an oil which could not be crystallized by separation from various solvents and was therefore boiled with methanolic sulphuric acid. Fractionation of the esterified product yielded a substance, b.p. about 65° C./2.5–3 mm., which crystallized in the condenser. This melted at 98–99° C. and when mixed with an authentic specimen of

methyl fumarate, m.p. 100–101° C., caused no depression in melting point. Small amounts of higher boiling fractions were also obtained, but in too small a quantity to permit identification.

Isolation of 3:4–methylenedioxyphthalide

From the potassium carbonate solution a mixture of oily substances was obtained which was boiled with methanolic sulphuric acid. This seemed to remove an oily impurity and the product on distillation yielded an oil, b.p. 164–5° C./3.5 mm., which on standing deposited a very small quantity of acicular colorless crystals which, recrystallized from methanol (charcoal) and from ether, melted at 225–226° C. The oil from which the above substance had separated crystallized when cooled, but melted again at room temperature. It apparently consisted of a mixture of methyl oleate and stearate (b.p. 150–152° C./3 mm.). The residue left in the distilling flask was dissolved in methanol (charcoal) and the solution allowed to stand, when it slowly deposited a further quantity of the same crystalline substance as above, melting at 225° C.

The sodium hydroxide extract yielded a dark green oil which was easily dissolved in methanol and boiled with sulphuric acid. The oily product was dissolved in ether and the solution washed with sodium bicarbonate and water, dried and evaporated. It yielded an oil which separated on cooling from solution in a mixture of ethyl acetate-methanol as long, colorless needles, m.p. 229–230° C. This substance, which is the same as that obtained from the potassium carbonate solution, is identical with 3:4–methylenedioxyphthalide isolated by Manske (1) from one of the products of the hydrolytic oxidation of the alkaloid adlumine. Admixed with a small quantity of the latter it began to sinter at 229° and melted completely at 232–233° C. The melt had crystallized again on cooling at 226° C.

Isolation of a Phytosterolin

That part of the original ether extract which was sparingly soluble in that solvent was digested with hot dioxane and the filtered solution allowed to cool. A white, crystalline substance gradually separated which was recrystallized from a mixture of dioxane and alcohol (charcoal), m.p. 295° C. Calcd. for $C_{33}H_{56}O_6$: C, 72.25; H, 10.21%. Found: C, 72.33, 72.17; H, 10.12, 10.24%. The interaction of benzoyl chloride with the substance in pyridine solution forms a tetrabenzoate, m.p. 184–5° C. (calcd. for $C_{33}H_{52}O_6(CO.C_6H_5)_4$: C, 75.9; H, 7.5%; found: C, 76.26; H, 7.74%), and boiling with acetic anhydride containing a small amount of pyridine yields a tetracetate, m.p. 157° C. Calcd. for $C_{33}H_{52}O_6(COCH_3)_4$: C, 68.7; H, 8.9%. Found: C, 69.31; H, 9.11%. The compound, which gave positive color tests, is undoubtedly a phytosterolin. Inasmuch as adlumiasterol is the only sterol found in the unsaponifiable fraction it was interesting to determine what sterol formed a constituent part of the sterolin. To this end 0.2 gm. of the sterolin was hydrolyzed in amyl alcoholic solution with aqueous hydrochloric acid according to Power and Salway's method (2). The amyl alcohol was

removed in a current of steam and the precipitated sterol filtered and recrystallized from a boiling mixture of methanol and ethyl acetate (charcoal) from which it separated in pearly flakes, m.p. 135–136° C. Admixed with the sterol obtained by hydrolysis of a sterolin isolated from the seeds of *Asclepias syriaca*, it melted at 135° C. Hence, the sterol constituent of the sterolin is quite different from that occurring in the free condition. The aqueous filtrate on treatment with phenylhydrazine yielded phenylglucosozone, m.p. 205° C.

Isolation of Adlumine and Adlumidine

The dioxane-alcohol mother liquors from the first crystallization of the phytosterolin, when further concentrated, yielded orange-colored prisms which, recrystallized from a mixture of acetone and methanol, separated in light yellow prisms, m.p. 237° C., was identical with adlumidine, $C_{19}H_{17}O_6N$. Admixture with an authentic specimen failed to cause any depression in melting point.

In the course of the extraction of the ether solution with 5% aqueous potassium carbonate as already mentioned, a white substance separated as glistening flakes. This, when recrystallized from dilute alcohol, yielded long slender needles which, after several recrystallizations, melted at 179° C. It was identical with adlumine and when admixed with an authentic specimen still melted at 179° C.

Chloroform Extract

The chloroform extract was filtered and shaken successively with 5% aqueous solutions of ammonium carbonate, sodium bicarbonate and sodium hydroxide. None of these aqueous extracts, however, yielded anything crystalline.

Isolation of Protopine and Bicuculline

The chloroform solution was then reduced to about 250 cc. and poured into an equal volume of ether which caused the separation of some gummy material. This was filtered out and the purplish fluorescent filtrate deprived of solvent, the oily residue dissolved in boiling methanol (charcoal) and the solution allowed to cool. The yellow crystalline material which was deposited was recrystallized from acetone-methanol and found to consist of adlumidine, m.p. 237° C. The methanol mother liquor on further standing deposited a mixture of very small crystals, large truncated octahedra and stellate aggregates of prismatic needles, which were separated mechanically and recrystallized. The respective substances were found to consist of the alkaloids adlumidine, adlumine, m.p. 180° C., and protopine $C_{20}H_{19}O_5N$, m.p. 209° C.

From the accumulated mother liquors a residue was obtained which yielded the alkaloid bicuculline, $C_{20}H_{17}O_6N$, m.p. 176–177° C. Hence, no non-basic substances were present in the chloroform extract.

Ethyl Acetate and Methanol Extracts

These extracts yielded only non-crystallizable solids resembling lignin. They were boiled with 10% aqueous sodium hydroxide, acidified and extracted with ether but traces of oil only were obtained.

Acknowledgment

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

X. *DICENTRA OREGANA*, Eastwood[1]

By R. H. F. Manske[2]

Abstract

The examination of the alkaloids of *D. oregana* has yielded seven bases, one of which appears to be identical with *alkaloid* δ previously found in two other *Dicentra* spp. A second base has not been adequately characterized because of paucity of material and is referred to as *alkaloid* ε. The remaining five alkaloids which are well known are *dicentrine*, *glaucine*, *corydine*, *protopine*, and *α-allocryptopine*. The isolation of the last from a species of *Dicentra* is the first on record. Attention is called to the ratio of glaucine to dicentrine and its significance is discussed. The total yield of purified alkaloids was unusually high (over 3.0%).

The species of *Dicentra* under consideration was first described by Miss Alice Eastwood in the Proceedings of the California Academy of Science (1931, vol. 20, p. 144) and has not yet been listed in the Kew Index. It is therefore pertinent to quote in part from the above mentioned record.

"Perennial from thick, branching, scaly rootstocks; leaves glabrous and glaucous, ternately compound with the divisions pinnately dissected, ultimate segments confluent, laciniately dentate, blade 6–10 cm. long and broad, petioles 1–2 dm. long, dilated at base; scapes naked, 2–3 dm. high, striate; inflorescence terminal, nodding paniculate with the flowers closely clustered on filiform pedicels, bracts and bractlets filiform to linear-attenuate; sepals oblong-lanceolate, acuminate, striate, 6 mm. long, 2.5 mm. wide; corolla ovate-cordate, exterior petals ochroleucous with short spreading tips, inner with the exserted limb rose color; ovary smooth, shorter than the style."

"——— In the U.S. National Herbarium it is represented by a specimen collected by Thomas Howell at Waldo, Oregon, June 4, 1884, No. 3424. ———. Not only in the color of the flowers but in the pallid foliage, this species presents a quite different appearance of any of the numerous forms of the variable Dicentra formosa".

The material for the present investigation was collected with obvious care by a competent collector in Oregon. Nevertheless it was deemed necessary to have it properly authenticated and for this service the writer expresses his thanks to Dr. H. T. Güssow, Dominion Botanist, who in turn submitted it to Miss Alice Eastwood, Curator of the Herbarium of the California Academy of Sciences.

Chemically, *D. oregana* was found to conform to its botanical relationship with *D. formosa* (5) and *D. eximia* (4). Protopine, because of its ubiquitous occurrence in plants of the Fumariaceae family cannot be regarded as pointing to closer affinities within a genus. However, dicentrine, corydine and

[1] *Manuscript received April 19, 1934.*
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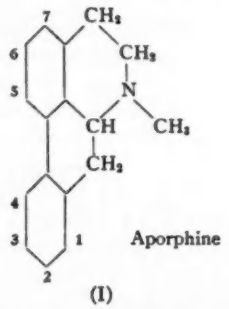
glaucine, particularly when all three occur in the one plant, indicate a chemical relation which in the three cases quoted is closely paralleled by botanical classification. The specificity of these three plants is nevertheless confirmed not only by the glaucine-dicentrine ratio (5), but by the appearance in each plant of one or more subsidiary alkaloids not common to the others.

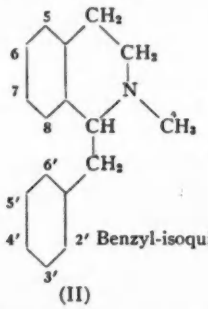
Though it has not been possible to obtain an accurate assay of both glaucine and dicentrine, the respective yields serve as a fair approximation. On this basis the ratio of glaucine to dicentrine is 100 : 64, and this in comparison with the corresponding ratios for *D. eximia* (100 : 1300) and *D. formosa* (100 : 70) points to an enhanced tendency to methylation as opposed to methylenation.

A second point of phytochemical interest emerges from an inspection of the nature of the aporphine bases. In the genus *Corydalis* these bases are derived from 3 : 4 : 5 : 6-tetrahydroxy-aporphine by partial methylation or methylenation or both. There are two obscure exceptions, namely, the occurrence of *d*-glaucine (2 : 3 : 5 : 6-tetramethoxy-aporphine)



Aporphine

(I)



Benzyl-isoquinoline

(II)

in the aerial portions of *C. cava* (1) and of *l*-glaucine in *C. ternata* (2). In the three *Dicentra* spp. under discussion however, the two types of aporphine bases (3 : 4 : 5 : 6- and 2 : 3 : 5 : 6-) occur side by side in quantities of the same order. Since the aporphine bases are probably derived from the 3′ : 4′ : 6 : 7-tetrahydroxy-benzyl-isoquinoline bases by oxidative ring closure at the 2′ : 8- or 6′ : 8- positions, the balance between the two types is certain to be a delicate one and slight changes of condition may have relatively large effects. Nevertheless, the catastrophic disappearance of one type or the other is difficult to conceive. The same is true of the ratio of methylation to methylenation products and the presence of allocryptopine (ratio to protopine, 100 : 210) in *D. oregana* is further evidence that the strong inclination to the former process is not confined to the aporphine bases, and that the specificity of this plant is assured. An abortive search for minute traces of alkaloids in the relatively small amounts of plant material available for these investigations cannot always affirm the complete absence of a particular base. With the proviso, however, that the absence of an alkaloid can be taken for granted when a special search has failed to yield it, allocryptopine can be stated to be

absent from *D. formosa*. On this basis corytuberine is not present in *D. oregana*, and its place is taken by an alkaloid which thus far has not been identified with any hitherto described. It is phenolic, probably contains two methoxyl groups, and yields analytical figures in fair agreement with $C_{19}H_{21}O_4N$ or with $C_{19}H_{23}O_4N$. Owing to the small amount available it will be referred to as alkaloid ϵ until adequate characterization is possible.

A seventh alkaloid was obtained in small amounts, and as far as identification has been possible it is regarded as identical with alkaloid δ first found in *D. eximia* and subsequently in *D. formosa*.

Experimental

There was available a total of 1515 gm. of dried plant material of which the roots constituted 1025 gm. The aerial portion and the roots were examined separately, but differences sufficient to place on record were not observed. The total yield of bases from the roots was however, slightly higher. The following record refers therefore only to the roots, and the designations of the various fractions are those of a previous communication (3).

Isolation of Dicentrine

Owing to the sparing solubility of the hydrochloride of this base it occurs not only in the fraction (BC), but the hot aqueous filtrate (S) and the aqueous filtrate (SR) frequently deposit the hydrochloride on cooling. In the present case these crops of hydrochloride were worked up separately. The fraction (BC) was again converted to hydrochloride and a further crop of dicentrine hydrochloride obtained in this way. The dicentrine was regenerated from this and the recrystallized base (m.p. 169° C.)* as well as the derivatives had the properties previously recorded (4). The yield of purified base was 0.76% which is appreciably higher than in any case on record.

Isolation of Glaucine

The free base was regenerated from the final dicentrine hydrochloride mother liquor by means of potassium hydroxide, gathered on a glass rod and thoroughly washed with water. The dried base was suspended in ether and the slight turbidity removed by filtration with the aid of charcoal. Evaporation to a thin syrup and addition of a crystal of *d*-glaucine induced immediate crystallization. After a convenient time the solid was filtered off, washed cautiously with ether (m.p. 117–118° C.) and recrystallized from boiling ether. Colorless crystals of *d*-glaucine were thus obtained, which alone, or admixed with specimens from *D. eximia* or *D. formosa*, melted at 120° C. It is difficult to obtain the last traces in a pure condition so that the yield of 1.19% is based on glaucine which was not of maximum purity.

Isolation of Corydine

The fraction (EC) was dissolved in methanol, treated with a slight excess of methanolic hydrogen chloride and the solution repeatedly evaporated with chloroform.

**Melting points are corrected.*

During the evaporation a sparingly soluble hydrochloride crystallized out. It was filtered off and washed with cold chloroform. The base was regenerated from this by treating a rapidly cooled aqueous solution with ammonia and extracting with ether. The ether extract on evaporation to a small volume deposited colorless triboluminescent prisms which melted at 120–122° C. either alone or admixed with a specimen of corydine similarly prepared from *D. eximia*. Although the rigorous identification which was recorded in the case of corydine from *D. formosa* was not repeated in this case, comparison with authentic specimens, and the properties of the hydrochloride, together with the general behavior, are considered sufficient. The yield was 0.05%.

Isolation of Alkaloid ε

This base was found in two fractions (EC) and (EEC). Had the extraction of the alkaline filtrate (FC) been more exhaustive it would probably not have been found in the latter fraction. This was dissolved in a mixture of chloroform and methanol, and the filtrate (charcoal) repeatedly evaporated with methanol. The somewhat concentrated solution deposited stout colorless prisms which melted at 220–222° C. with some previous sintering. After two further recrystallizations from chloroform-methanol the base melted at 230°, sintering beginning at 224–225° C.

It was also obtained from fraction (EC). For this purpose the chloroform mother liquor from the corydine hydrochloride was freed of solvent, the residue dissolved in water and the clarified filtrate basified with excess potassium hydroxide. The resulting turbidity was removed by filtration and the filtrate saturated with ammonium chloride. Ether then removed a small amount of base which when recrystallized from methanol melted with previous sintering at 228° C. Admixture with the base from fraction (EEC) did not lower the melting point. The combined yield was 0.01%.

The micro-Zeisel determination of methoxyl gave figures rather too high for two such groups. On the other hand the results for the combined methoxyl- and methylimino- groups are in fair agreement with two of the former and one of the latter.

Calcd. for $C_{19}H_{21}O_4N$: C, 69.74; H, 6.40; N, 4.28; 2OMe + NMe as OMe, 28.34%. Found: C, 69.67, 69.87; H, 6.70, 6.79; N, 4.13, 4.28; OMe + NMe, 27.25%.

Examination of fraction (BCE) for corytuberine failed to show its presence (5).

Isolation of Protopine

The fraction (BS) was dissolved in chloroform and the filtered solution (charcoal) repeatedly evaporated with methanol. The hot solution was inoculated with a crystal of protopine and rapid crystallization induced by shaking. The protopine (m.p. 208° C.) was filtered off, washed with methanol, and the combined filtrates evaporated to a thin syrup. A second crop of protopine was obtained. The combined yield was 0.71%. A recrystallized

specimen was authenticated by color reactions and mixed melting point determination (211° C.).

Isolation of α-Allocryptopine (β-Homochelidonine)

The methanolic filtrate from the crystallization of the protopine was evaporated to a small volume, neutralized with methanolic hydrogen chloride, and inoculated with a crystal of protopine hydrochloride. The small amount of the latter, which crystallized in the course of several days was filtered off and the filtrate poured into water. The methanol was boiled off and the filtered and cooled solution basified with excess potassium hydroxide. The granular precipitate was filtered off, washed, dried, and dissolved in chloroform. The filtered solution was repeatedly evaporated with methanol, finally to a thin syrup. To the latter a large volume of dry ether was added and the small amount of amorphous residue removed with the aid of charcoal. The clear filtrate was evaporated to a syrup. In the course of several days a single crystal nucleus had appeared. The addition of a little methanol and rubbing with a glass rod induced the crystallization of a copious crop of alkaloid which melted not quite sharply at 157–158° C. Small amounts of protopine were still present, but rapid solution in boiling methanol left the greater portion undissolved and the base which crystallized from the filtrate melted at 159–160° C. A repetition of the process yielded the pure base melting at 160–161° C. A crystal dissolved in acetic acid and treated with concentrated sulphuric acid developed a rich reddish-violet color. The β-form was not obtained. Gaebel's test for the methylene-dioxy group was positive though not nearly as intense as a comparative test with protopine. The yield was 0.33%. Calcd. for $C_{21}H_{23}O_5N$: N, 3.80; OMe, 17.17%. Found: N, 3.82, 3.82; OMe, 15.57, 14.50%.

Isolation of Alkaloid δ

This alkaloid, which has thus far not been obtained crystalline in the free condition, was isolated as the hydrochloride from the fractions (BSE) and (EES) in the manner recorded previously (4, 5). The criteria of identity have been,—the properties of the hydrochloride (no change in melting point on admixture), color reactions with sulphuric acid, and induction of crystallization of one salt in supersaturated solution by another. No observation which would serve to distinguish one from the others has been made. The yield of hydrochloride (m.p. 236–237° C. dec.) was somewhat less than 0.01%.

Isolation of Fumaric Acid

With the one exception of the tubers of *D. canadensis*, all plants which have come under this program of chemical examination have yielded fumaric acid in varying amounts. The fraction (LC) in the present investigation yielded less than 0.01%, but nevertheless, there was sufficient for proper identification after it was repeatedly recrystallized from water. It melted either alone or admixed with an authentic specimen of fumaric acid at 287–288° C. (uncorr.).

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THE PREPARATION AND QUALITATIVE IDENTIFICATION OF 2,5-DIMETHYLPYRROLE[1]

By C. F. H. Allen[2] and D. M. Young[3]

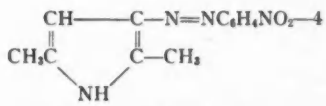
Abstract

A new and convenient method for preparing 2,5-dimethylpyrrole, by the interaction of acetonylacetone and ammonium carbonate, is described. It may be identified by the formation of three solid derivatives: (*a*) the azo compound; (*b*) the mono-2,4-dinitrophenylhydrazone of acetonylacetone; and (*c*) its condensation product with acetone.

The recent accessibility of acetonylacetone has made it possible to obtain hitherto uncommon substances in the heterocyclic series of five membered rings for investigation. Among these is 2,5-dimethylpyrrole. This substance has always been prepared from the diketone by the action of ammonia under pressure; the yields are about 50% (3, 6). By substituting ammonium carbonate, it is now readily obtained in any quantity in the usual laboratory apparatus.

The recognition of 2,5-dimethylpyrrole has been based on physical properties; the non-formation of characteristic solid derivatives is both unsatisfactory and inconvenient. If it reacts with halogen acids, picric acid, alkyl halides, and methyl *p*-toluene sulphonate, it does not give solid derivatives. It does not add maleic anhydride when mixtures are heated, either alone or in benzene.

Three reactions that are useful for identification have been found. First, the pyrrole couples with *p*-nitrodiazobenzene chloride. The azo compound



has been described previously (5). Second, it reacts very rapidly with 2,4-dinitrophenylhydrazine in the presence of dilute mineral acid, to give the mono-2,4-dinitrophenylhydrazone of acetonylacetone; this is essentially a reversal of the method of preparation of the pyrrole. The ease of opening of the pyrrole ring in this instance is noteworthy, but in agreement with the formation of the dioxime of acetonylacetone by the action of alkaline hydroxylamine on 2,5-dimethylpyrrole (1). There is very little in the literature on this and analogous reactions; prolonged boiling with alkaline hydroxylamine eventually yields small amounts of succindialdehyde dioxime with pyrrole, while 2,5-dimethylpyrrole and nitrous acid give the 2,3-dioxime of 1,4-dimethyltetraketone (4). No dinitrophenylhydrazone formation was noted with pyrrole, or 2,4-dimethyl-3,5-dicarbethoxypyrrole, even on long heating of the reactants; 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole gave a dinitro-

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phenylhydrazone, presumably of the methyl ketone, since the ring nitrogen was still present. Third, in the presence of hydrochloric acid, 2,5-dimethylpyrrole and acetone form a crystalline substance of unknown structure, $C_{18}H_{26}N_2$ (6), when operations are performed in a particular manner.

Experimental

Acetonylacetone* (100 gm.) and 200 gm. of U.S.P. ammonium carbonate in lumps are placed in a 500 cc. Erlenmeyer flask, fitted with a large bore reflux condenser. The mixture is heated in an oil bath at 100° C. until effervescence stops (one hour) and refluxed a further half hour at 115° C. When cool, the upper pyrrole layer is separated and dried overnight with anhydrous calcium chloride in a stoppered flask, previously swept out with nitrogen. (From this point on, all manipulations must be done in an oxygen-free atmosphere.) It is then vacuum-distilled; the moist fore-runnings are collected separately, but the fraction boiling at 50–53° C. at 8 mm. (165–167° C. at 760 mm.) is retained. The average yield in a number of runs was 72 gm. or 87%. The product has a very slight yellowish tinge which gradually becomes red—this change is accelerated by light and air, so the pyrrole is best preserved under nitrogen in a brown glass container. The refractive index of the freshly distilled material is $1.5001_D^{22°}$; Nasini and Carrara give $1.5036_D^{19.8°}$ (2). Under the same conditions, 2,5-dimethylfurane does not react with ammonium carbonate, and is recovered unchanged.

Derivatives

(a) The azo compound. A solution of diazotized *p*-nitraniline is added to a cold mixture of 1 gm. of dimethylpyrrole in 5 cc. of acetic acid; the reddish-orange precipitate must be filtered at once to avoid decomposition. It is boiled a few minutes with 15–20 cc. of ether, filtered, washed with the same solvent and dried. It forms carmine needles that shrink suddenly at about 165° C. and melt to a liquid at about 200° C.; the analysis indicates a dihydrate. Calcd. for $C_{23}H_{12}O_2N_3 \cdot 2H_2O$: N, 20.0%. Found: N, 20.1%. For purification it is dissolved in about 10 cc. of hot methyl alcohol and on addition of water, reddish-brown microscopic needles are precipitated. These crystals melt with decomposition at 208–212° C., according to the rate of heating. Since the melting point varies in this way, it is advisable to prepare an additional derivative, such as is described below. Three drops of the pyrrole is the minimum that can be detected by this procedure, with certainty.

(b) Mono-2,4-dinitrophenylhydrazone of acetonylacetone. A mixture of 0.5 gm. of 2,4-dinitrophenylhydrazine, 0.25 gm. of 2,5-dimethylpyrrole, and 25 cc. of 95% ethyl alcohol is heated to the boiling point and 1 cc. of 10% sulphuric acid added. An orange precipitate separates at once; it is filtered and recrystallized from pyridine, from which it separates in orange needles, m.p. 262° C. It is insoluble in the common organic solvents, except nitrobenzene, and in butyl alcohol, dioxane, cymene, 2,5-dimethylfurane, and amyl ether.

The diketone used was supplied by Shawinigan Chemicals, Limited, and is gratefully acknowledged.

Calcd. for $C_{12}H_{14}O_5N_4$: N, 19.0%. Found: N, 18.8%. It is identical with the derivative formed from acetonylacetone by the same procedure.

The 2,4-dinitrophenylhydrazone of 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole was prepared in the same manner. It crystallizes in carmine rods from aniline, m.p. 264° C. Calcd. for $C_{17}H_{19}O_6N_5$: N, 18.0%. Found: N, 17.6%.

When pyrrole or 2,4-dimethyl-3,5-dicarbethoxypyrrole was treated by the same procedure, or much more drastically, the reagent and pyrrole ester were recovered unchanged; the unsubstituted pyrrole resinified.

(c) To a mixture of 2.5 cc. of 2,5-dimethylpyrrole and 8 cc. of acetone at room temperature are added four drops of concentrated hydrochloric acid. After five minutes the solution is poured into 20 cc. of water, the precipitate filtered, and recrystallized from 50% alcohol. It forms flesh-colored needles, m.p. 174° C., after two recrystallizations. Calcd. for $C_{18}H_{26}N_2$: N, 10.4%. Mol. wt. 270. Found: N, 10.9%. Mol. wt. 269. Slight variations lead to other products, but as little as 0.5 gm. of the pyrrole can be detected by the above procedure. The substance is not obtained when acetonylacetone is substituted for the pyrrole, nor when the acetone is replaced by diacetone-alcohol or mesityl oxide.

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THE RELATION BETWEEN YIELD AND PROTEIN CONTENT OF WHEAT[1]

By J. G. Malloch[2] and R. Newton[3]

Abstract

A significant inverse relation was found between yield and protein content, more pronounced in 1930 than in 1931. Reduction of yield by removing tillers or heads increased the protein content in both these years and the weight per 1000 kernels in 1930. Grade and kernel texture were unaffected by this pruning.

Introduction

Yield and protein content are the most important characters of Canadian wheat, the former because of its direct effect on the farmer's revenue and the latter because of its relation to baking quality. Unfortunately, when wheat is grown under climatic conditions favoring high yield the protein content is usually low. Climate, however, is not the only factor affecting these characters, since it is well known that the yield will vary markedly in different parts of the same field and similar variations in protein content have been shown to occur (4). Waldron (5) has reported an inverse relation ($r = -0.556$) between the yield and protein content of 25 varieties of wheat grown in replicated plots in a single field. The experiments reported in this paper were designed to test the relation between yield and protein content of a single variety as affected by variations in the soil and by pruning the plants. The grade and weight per 1000 kernels were studied concurrently.

Effect of Soil Heterogeneity

The effect of soil heterogeneity on the yield and protein content of wheat was measured in 1930 and 1931. In both years the field selected was reasonably level and did not show any obvious variations in soil. The crop was a pure line of Red Bobs 222 in 1930 and of Marquis in 1931 so that variation in inherited characters was reduced to a minimum. Just prior to the harvesting of the main crop, fifty 18-ft. rows were cut by hand at locations scattered over the field. The field used in 1930 was approximately 14 by 34 rods; and that used in 1931 about 8 by 62 rods in size. Each 18-ft. row was threshed separately, the yield recorded and the grain preserved for protein determinations. The data are given in Table I and the statistical constants calculated from them in Table II.

It will be seen that yield was more variable than protein content and that the variation in yield was more pronounced in 1931 while the protein content varied more in 1930. The correlation and regression coefficients are significant.

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The significance of the difference between the values of r for the two years may be determined by means of the transformation due to Fisher (1, p. 182). The difference between these transformed values is 0.39 with a standard error of 0.206; this, though suggestive, cannot be regarded as unquestionably significant. The difference in the regression coefficients for the two years is 0.00475 with a standard error of 0.00131 giving a t value of 3.642, and therefore, is definitely significant.

TABLE I

YIELD (gm.) AND PROTEIN CONTENT (%, 13.5% MOISTURE BASIS) OF WHEAT FROM 18-FT. ROWS

Yield	Protein	Yield	Protein	Yield	Protein	Yield	Protein	Yield	Protein
				1930					
243	14.1	344	14.9	400	13.5	445	13.4	463	14.1
424	14.4	349	14.4	444	13.0	339	14.9	390	14.5
305	14.8	228	15.7	300	15.1	314	14.6	433	14.5
322	14.4	377	14.9	296	15.3	230	15.3	483	12.5
413	14.3	300	15.0	360	15.0	235	15.1	330	14.2
323	14.7	252	15.4	294	15.3	218	15.1	294	14.6
235	15.5	286	14.9	232	15.5	262	15.2	310	15.3
182	15.3	273	14.2	246	14.9	238	14.8	208	16.7
137	16.2	228	15.6	253	14.3	259	15.1	270	15.8
255	12.9	145	16.5	318	14.7	249	14.5	321	15.7
				1931					
223	13.3	501	13.7	393	14.3	304	14.0	514	14.5
373	14.3	175	13.9	319	14.2	306	13.5	229	14.7
303	14.1	349	12.9	314	14.4	178	14.4	151	14.7
342	14.8	303	14.2	185	14.5	294	14.1	193	15.4
298	14.7	297	15.1	94	15.0	236	14.1	181	14.6
373	13.6	232	14.7	164	15.4	212	14.5	178	14.2
426	14.5	45	14.8	239	14.6	273	14.8	234	14.8
419	14.0	143	14.7	90	15.0	226	14.8	262	14.6
376	13.6	357	14.4	353	14.4	418	14.4	230	15.2
326	12.9	363	14.1	342	14.0	390	14.1	316	15.3

Thus the correlation coefficients indicate that high yield was associated with low protein content, though less regularly in 1931 than in 1930. While this difference in closeness of association in the two years was just below the level of statistical significance, the data are not extensive enough to warrant a conclusion that the degree of association is

TABLE II

STATISTICAL CONSTANTS
(Data from Table I)

——	1930	1931
Average yield (gm.)	301	281
Standard error	80.3	102.2
Average protein (%, 13.5% moisture basis)	14.8	14.4
Standard error	0.83	0.56
Correlation (r)	−0.68	−0.42
1% point for 47 pairs	0.37	0.37
Regression (b)	−0.00709	−0.00233

statistically constant, and further experiments might easily produce significant differences. The regression coefficients show quite definitely that the amount by which a given change in yield affects protein content varies from year to year. In 1931, the decrease in protein content with increased yield was significantly less than in 1930.

Effect of Pruning to Reduce Yield

While both climate and soil, as well as other factors, such as varietal differences and irregularities in seeding, play a part in modifying the relation between yield and protein content in different seasons, the variations found in different parts of a level field in one season must depend mainly on soil differences. Of the principal nutrient substances, nitrates may be expected to exert the chief influence. Gericke (2) showed that yield and protein content are affected by the time at which nitrates become available. This depends largely on the relative rates of nitrification at different stages of plant growth. Nitrates may be used to build up the vegetative parts of the plant or for kernel formation. Since the weight of kernels produced is closely related to the amount of vegetative growth it follows that if the supply of nitrates in the soil is constant, any factor which depresses vegetative growth is likely to raise the protein content.

An experiment designed to test the above hypothesis was conducted concurrently with the experiment just reported. It was assumed that removal of parts of the top of the plant would not affect root development to any marked degree and that therefore the artificial reduction of yield by pruning should lead to a higher proportion, in the remaining grain, of materials absorbed from the soil. It is impossible to eliminate entirely variations in the supply of nitrates to each plant, but by use of small plots and the concentration of the experiment on a small area the chances of major variations are reduced. Further, by replication of the treatment in four blocks of plots and the arrangement of the plots in each block at random, only such soil heterogeneity as occurs within blocks will affect the treatment comparisons.

The treatments used, together with a short title for each, are given below:

Check—No treatment.

Tillers removed—All but two tillers were removed from each plant when normal tillering was completed and second growth tillers were cut back throughout the growing season.

Heads removed at flowering—All but two heads were removed at the time the upper heads were in flower. Any heads which appeared subsequently on late tillers were removed.

Heads removed in milk stage—All but two heads were removed when the kernels of the upper heads were in the milk stage.

The plots were arranged in four blocks, each treatment occurring once in each block. Each plot consisted of three rows 2 links apart, 29 links long in 1930 and 37 links long in 1931. As soon as all the plants had emerged the centre row of each plot was thinned until the plants were two inches apart.

The treatments were applied to the centre rows only. At harvest a 2-link border was removed from the ends of the plots and the centre rows were cut and threshed separately.

Protein Content

The protein content of the grain is shown in Table III and the statistical constants calculated from these results in Table IV.

The variance due to treatment and also to the interaction "Years × Treatments" significantly exceeds the error variance. The treatment variance, however, is not significantly greater than the foregoing interaction. In other words, pruning the plants definitely affected the protein content of the grain but the relative effect of the treatments was not the same in the two years of the experiment. The necessary difference between the means of four plots was calculated from Table IV and found to be 0.32. Turning to Table III, we find that in 1930 all of the treatments gave protein contents significantly higher than that of the check plots. Removal of tillers and removal of heads at flowering time increased the protein more than removal of the heads in the milk stage. The results in 1931 were different in character. Removal of the heads at flowering time did not increase the protein content significantly. The removal of tillers gave increased protein though not to the same extent as in 1930. The increase due to the removal of heads in the milk stage was identical in the two years. In 1931 there was not the significant difference between the treated plots that there was in 1930.

These results show that reduction in yield by pruning will increase the protein content, thus supporting the initial hypothesis. It should be noted that the pruned rows were in close proximity to rows of normal plants. It is possible that competition deprived the treated plants of part of their share of nutrients. The effects obtained can therefore be regarded as minimal.

TABLE III

EFFECT OF PRUNING ON PROTEIN CONTENT
(%, 13.5% MOISTURE BASIS)

	Check	Tillers removed	Heads removed at flowering	Heads removed at milk stage
		1930		
Block 1	15.6	16.3	16.6	15.6
Block 2	15.0	16.5	16.4	15.7
Block 3	15.1	16.3	16.0	15.7
Block 4	15.3	16.3	17.1	15.6
Average	15.2	16.3	16.5	15.6
		1931		
Block 1	14.3	14.7	14.7	14.9
Block 2	14.5	15.0	14.8	14.8
Block 3	14.8	15.2	14.8	15.3
Block 4	14.6	15.0	14.5	14.7
Average	14.5	15.0	14.7	14.9

(Necessary difference in yearly averages = 0.32.)

TABLE IV

ANALYSIS OF VARIANCE
(Data from Table III)

	Degrees of freedom	Sum of squares	Mean square	Z value	
				Calculated	At 5% point
Years	1	10.69	10.69	—	—
Blocks	6	0.56	0.093	—	—
Treatments	3	2.97	0.990	1.528	0.8138
Years × Treatments	3	1.79	0.597	1.275	0.8138
Error	18	0.84	0.0466	—	—
Total	31	16.85			

Kernel Texture and Grade

The variations in protein content were not reflected in the appearance of the kernels. In the two years of the experiment there was only one sample which had less than 99% vitreous kernels and this contained 96.5%. The official grades in 1930 varied from 1 Hard to 2 Northern, the majority of the samples being classed as 1 Northern. In 1931 the samples all graded 2 or 3 Northern. The differences in grading are attributable to differences in the maturity of the samples and therefore are irrelevant to the present discussion.

Weight per Thousand Kernels

Since the pruned plants were arbitrarily limited to two heads each, the vigor of vegetative growth could not be expressed in terms of total yield of grain. However, since the average number of kernels per plant would be nearly constant for all treatments, the weights per 1000 kernels may be taken as a good indication of vegetative vigor. These are given in Table V.

TABLE V

EFFECT OF PRUNING ON WEIGHT PER 1000 KERNELS
(gm.)

	Check	Tillers removed	Heads removed at flowering	Heads removed at milk stage
1930				
Block 1	36.8	42.8	36.7	38.2
Block 2	34.4	38.2	39.5	32.1
Block 3	36.9	42.7	37.4	36.8
Block 4	35.4	39.1	39.2	37.8
Average	35.9	40.7	38.2	36.2
1931				
Block 1	33.3	33.1	34.1	34.2
Block 2	29.7	30.2	30.0	32.3
Block 3	28.7	26.2	27.3	27.4
Block 4	33.3	32.0	29.7	31.4
Average	31.2	30.4	30.3	31.3

It does not require a statistical analysis to show that the differences in 1931 were not significant. The results for 1930 were however subjected to an analysis of variance, reported in Table VI. This shows that the treatments

had a significant effect in 1930, the necessary difference in weight per 1000 kernels being 1.46. Those plants from which tillers or heads had been removed at flowering gave heavier kernels than the plants in the check plots. The difference between the plants treated in the milk stage and the checks is not significant.

TABLE VI

ANALYSIS OF VARIANCE
(Weight per 1000 kernels, 1930)

	Degrees of freedom	Sum of squares	Mean square	Z
Blocks	3	16.64	5.55	0.1891
Treatment	3	58.98	19.66	0.8218
Error	9	34.20	3.80	
Total	15	109.82		

The treatments which gave significant increases in weight per 1000 kernels are those which gave the greatest increase in protein content. It is evident therefore that pruning affected the protein content by greatly increasing the nitrogen supply to the remaining kernels rather than by interference with the deposition of carbohydrates. The results show that conditions which favored nitrogen supply to the greatest degree also favored the laying down of carbohydrates, since the increase in weight of the kernels cannot be entirely accounted for by the increased weight of protein. The correlation between yield and protein in the first experiment and the effect of pruning on protein and on weight per 1000 kernels were all greater in 1930 than in 1931.

The results of these two experiments support the common observation referred to in the introduction that usually there is an inverse relation between yield and protein content. This does not mean however that yield can only be increased at the expense of a decrease in protein content. Under suitable conditions there can be a concurrent increase in both yield and protein (3). In any study of cultural practices for wheat their effect on protein content as well as on yield should be considered.

Acknowledgment

We are indebted to Mr. J. W. Hopkins of the Division of Biology and Agriculture, National Research Council, for his assistance with the statistical analysis of the data.

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IS *RORIDULA* A CARNIVOROUS PLANT?[1]

By Francis E. Lloyd[2]

Abstract

The genus *Roridula* has two species, the leaves of both of which are armed with numerous glands secreting a "balsam"-like exudate, whereby many insects are captured, simulating in this the behavior of *Drosera*, *Drosophyllum* and *Byblis*. . But as Marloth held, these plants are not carnivorous.

Living "commensally" on both species are at least five different insects, three crab-spiders and two capsids (true bugs). All these can move about freely on the *Roridula* plants without danger of capture; they gain their livelihood by sucking the juices of freshly captured insects.

The structure of the glands of these plants and the nature of their secretion are described.

The immunity of the insects above mentioned from capture is attributed to the character of the surface of the resinous secretion, to the spiny surface of the insects, which prevents the presentation of extensive surfaces for adhesion and to the ability of the insects to negotiate their environment. The argument is not held to be conclusive but suggestive; and the matter is worthy of further study.

Under the above title a brief report was offered at the Leicester meeting of the Section of Botany, British Association for the Advancement of Science, and an answer given in the negative. It is the purpose of the present paper to give the evidence in support of that answer. That this is not superfluous is indicated by the fact that in general accounts *Roridula* is still cited as one of the relatively few carnivorous plants. Thus Quintanilha (8, Plate I) includes it in his roster. I had done so myself (4, Plate 16) but for the timely reception of material kindly afforded me by Professor von Wettstein of Munich, from the examination of which I found that the secretion of the glands is a resinous one,* and that their structure, hitherto incorrectly described by both Fenner (3) and Bruce (1, Plates 20, 21), is very different from that of the glands of *Drosera*. The veteran South African botanist, the late Dr. Marloth, who in later years came to the position that *Roridula* is not carnivorous, thought indeed that its inclusion in the Droseraceae is traceable to the general similarity of the plants to *Drosera*, and especially of the glands. As the genus is South African, with only two species, and is in general but little known, there has been little careful examination made of it, especially as it has only seldom been introduced into glasshouse cultivation. At the present moment, material of the two species may be found growing, so far as I know, only in the glasshouses of the Botanical Institute in Munich. It was this happy circumstance that enabled me to direct my own observation to specimens of both species (Plate I–1, 2) during the summer of 1933. Not only to specimens of the plants alone, however, but to one (Plate I–3) of the several species of insects that habitually live complacently on them without suffering the indignity of capture which overtakes other adventurous insects.

[1] *Manuscript received April 11, 1934.*
Contribution from the Department of Botany, McGill University, Montreal, Canada.

[2] *Macdonald Professor of Botany, McGill University.*

**The secretion persists as pellucid droplets indefinitely on dead and dried-up leaves, as Bruce (1) observed.*

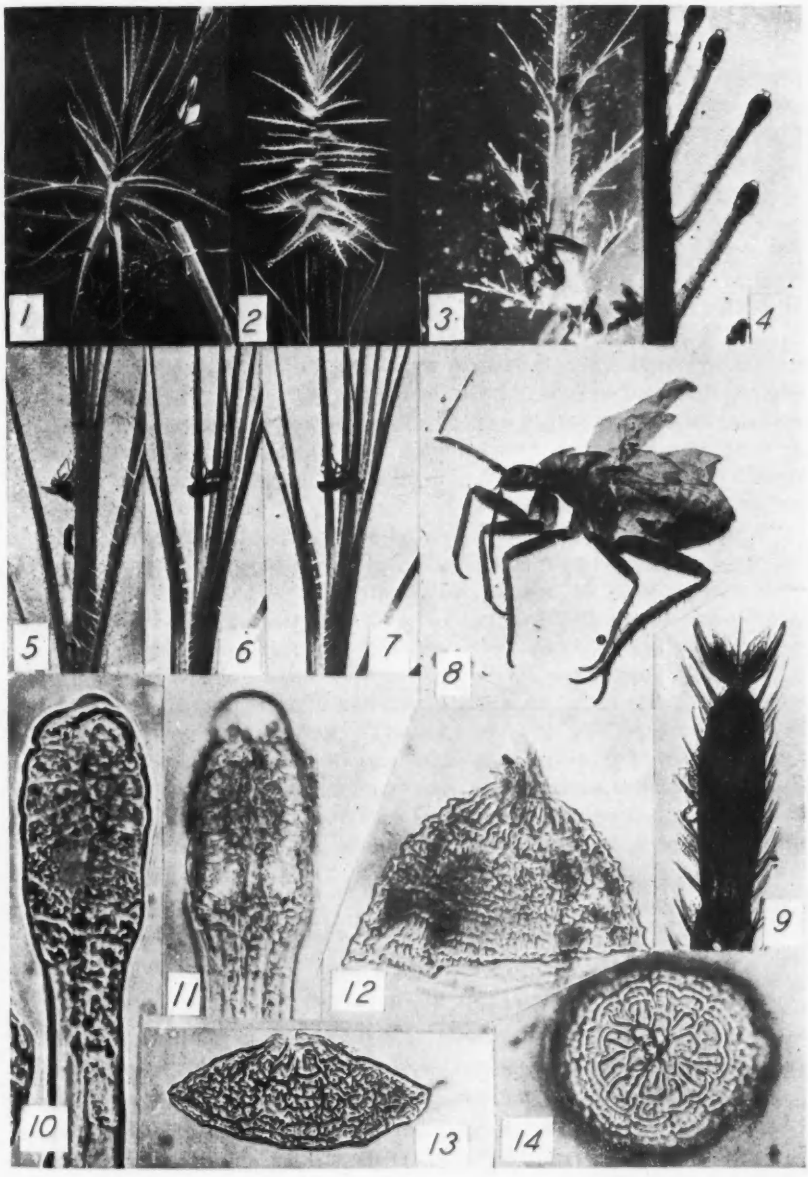

Fig. 1. *Roridula gorgonias. A capsid may be seen standing on one of the upper leaves.* FIG. 2. *R. dentata.* FIG. 3. *Portion of a leaf of R. dentata with a capsid (Pameridea sp.), for visualization of relative sizes. The insect was not alive.* FIG. 4. *Portion of leaf margin of R. dentata, with droplets of the secretion on the apices of the glands. The translucent spots near the bases of the glands indicate the secretion held in their canals.* FIGS. 5, 6 and 7. *Three views of the upper leaves of R. gorgonias showing a recently caught fly and a living capsid approaching, and in different positions sucking the juices of the prey.* FIG. 8. *The capsid in question, Pameridea sp.* FIG. 9. *A foot of this insect showing that all its parts are sharply pointed.* FIG. 10. *A small gland in optical section which shows the zone of large wedge-shaped cells near the base.* FIG. 11. *A small gland (but larger than that in Fig. 10), with the optical plane near the surface, showing a zigzag canal and the translucence produced by the resinous contents of the laterally viewed canals.* FIG. 12. *The cuticle removed from the apex of a large gland, showing the escape of cells destroyed by sulphuric acid through the apical pore.* FIG. 13. *The apex of a small gland showing the apical pore.* FIG. 14. *The apex of a medium-sized gland seen from above, showing the crown of cells surrounding the apical pore, which is obfuscated by the presence of three fragments of detritus of destroyed interior cells.*

I am indebted to the late Professor K. von Goebel and to his successor, Professor von Wettstein, for the privilege of working on this material.

The course of thought on the question is briefly as follows. Marloth in 1903 (7) inferentially admitted *Roridula* to be carnivorous in saying, "We find that *Roridula* catches insects to obtain an additional food supply, but that a spider robs the plant of a share of the prey in spite of the sticky tentacles." In the following year Fenner (3), basing his view on the structure of the glands as he understood it, regarded them as "wirkliche, typische Insekt-enfaenger"* and in this Bruce (1, Plates 20, 21) concurred. "v. Marloth bestritten" is a pencilled remark made by Goebel on a margin of Fenner's paper, referring to Marloth's later view expressed in his beautiful Flora of South Africa (6). Here Marloth observed that the inclusion of *Roridula* with the Droseraceae would appear to be due to its apparent insectivorous habit. The plants, he now averred, are however not insectivorous, since *(a)* there are no digestive organs on the leaves; *(b)* the glands† are quite different in structure from those of *Drosera; (c)* the secretion is not a slime with digestive properties but a kind of balsam which yields, when washed with chloroform, a very viscid residue which contains about 10% of caoutchouc; and *(d)* the capturing of insects is accidental and of no advantage to the plant.‡ He showed further that there are four kinds of insects "commensal" on these plants, these including two species of bugs of the genus *Pameridea* (Capsidae) of which *P. marlothii* is found on *R. dentata* and the other, *P. roridulae*, on *R. gorgonias*,** and two spiders on *R. dentata*, *R. gorgonias* apparently being free of them. These spiders are "crab-spiders" (*Synaema* spp.), well known as lying in wait for insects inhabiting inflorescences of various kinds. The species of *Pameridea* are, Marloth believes, responsible agents for pollination, for they suck juices from the swollen portion of the stamen which contains sugar, whereupon the anther swings into the position of pollination.

In the light of the above conclusions we may now examine the situation as understood at present.

Structure of the Glands

There is one kind of gland only. In *Drosera*, in addition to the tentacles, there are minute sessile glands (4) which Darwin (2) thought might be absorptive. They have not been studied§ and nothing definite can be said about them. If Marloth was thinking of these we can concur with him. But it is now generally agreed that the chief digestive activity resides in the large glands supported on the ends of the tentacles, which are superficially yet

**It was Fenner's meaning that Roridula is a typical carnivorous plant; Goebel evidently so thought.*

†Marloth's figure was taken from Fenner.

‡Bruce's experiments leading to the opposite conclusion were few, equivocal and unconvincing.

***The single species seen in Munich seems to show no preference for one species.*

§Except anatomically by Fenner.

strikingly similar (Fig. 2) to those of *Roridula* (Fig. 1). In this genus, as Fenner states, they may be small and of simple construction, consisting of four rows of epidermal secreting cells surmounting the supporting tentacle, which contains no vascular tissue (Fig. 1–*B*); or, in the extreme, there may be a considerable number (± 16) of longitudinal rows of secreting epidermal cells surrounding a core of regularly composed parenchyma of a number of

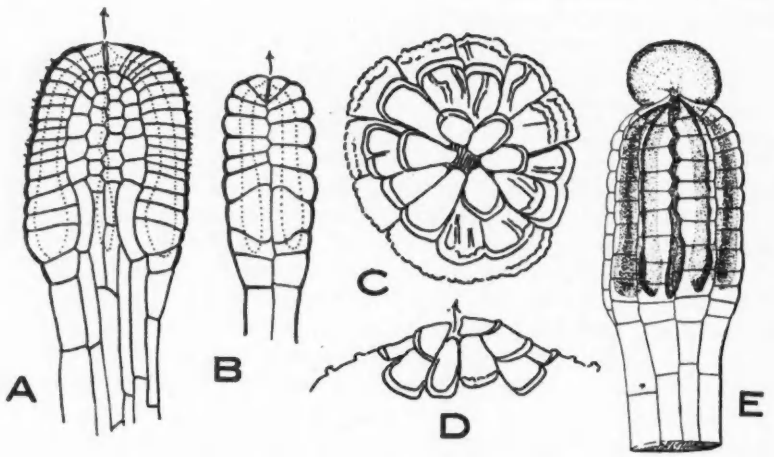

FIG. 1. *Roridula. A, Diagram of section of a large gland showing the core of parenchyma: the position of the resin canals is indicated by dotted lines, the middle canal seen as projected on the section (compare with E); B, section of a small gland with no core of parenchyma, resin canals indicated by dotted lines; C, apex of a gland seen from above; D, and as seen from the side; E, diagram of a medium sized gland of eight longitudinal series of epidermis cells. The extent of five of the resin canals is indicated by the stippled areas, also the secretion oozing from the apical pore.*

longitudinal series of cells according to the size of the gland (Fig. 1–*A*). The whole is covered by a thick cuticle (resistant to sulphuric acid), which displays much irregularity (ridging, folding) (Fig. 1), and in which he mistakenly believed there are pores suitable for the escape of the secretion, the nature of which escaped him. Another feature of structure was observed by him: that a transverse row of epidermal cells near the base of the gland is much deeper (in a longitudinal sense) than the neighboring, whereby the cells above and below are distorted, especially inwardly (Fig. 1 *A–B;* Plate I—10, 11).

In 1907, Bruce (1, Plates 20, 21) independently made a study of these glands and described the epidermal elements as being constricted in their middle, so that each cell was free of its neighbor except at top and bottom. Because each cell is constricted, both transverse and longitudinal sections of the glands show a circular intercellular space between adjacent cells. Now, as a matter of fact, this is true enough of the transverse section but not of the longitudinal, and Bruce was in error here.

The fact is, that between each two longitudinal series of epidermal cells there is a canal or duct which is much wider in the zone of the larger, near-basal cells, here forming, between each pair of large cells (which Bruce failed to see), a narrowly oval reservoir (in appearance), so that from the base of the gland there is a number of canals extending quite to the apex, in number equal to the number of series of epidermal cells (Fig. 1, *E;* Plate I—11). To complete this picture, there is at the apex of the gland a schizolytic opening through which the secretion, which fills the reservoirs and canals, escapes (Fig. 1; Plate I—12–14), demonstration of which I have already described (4, Plate 16). Because of the alternate emplacement of the hexagonal epidermal cells, the canals are always more or less zigzag (Fig. 1, *E;* Plate I—11). Escaping the observation in freshly mounted glands, the canals and reservoirs become readily visible after slight staining with Sudan III. It has been said that the epidermal cells are secretory and, by implication at all events, not the central parenchyma, but it is at the moment gratuitous to deny such activity to the central cells, in *Roridula* at least. It is perhaps less gratuitous to suggest that the major physiological activity in secretion is a function of the zone of wide cells against which lie the reservoir-like expansions of the resin canals (Fig. 1).

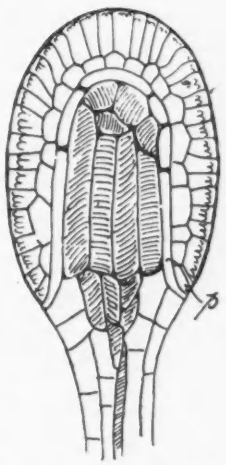

FIG. 2. *Section of the gland of Drosera for comparison with that of Roridula.*

The cases of *Drosera* and *Drosophyllum* are more convincing (3; 4, Plate 16).

Nature of the Secretion

Neither Bruce (who observed living plants at Edinburgh) nor Fenner suspected that the secretion was other than a watery slime. That this could not be the case I saw at once on examining leaves preserved in formalin, sent to me by Professor von Wettstein, for in this the drops of secretion were still intact, which had not been the case were it similar to that of *Drosera* (4, Plate 16). Simple tests showed the secretion to be of resinous nature. Marloth (6) had already examined it in this way, as above noted, finding a small proportion of caoutchouc.* Obtaining sufficient material at Munich, I extracted about a dozen leaves with acetone, which yielded a resin (or mixture of resins). The leaves were then extracted with petroleum ether by Dr. R. D. Gibbs, yielding an acetone insoluble material having properties of caoutchouc, so far as visible behavior indicated. We may thus agree with Marloth at least far enough to say that the secretion contains a caoutchouc or caoutchouc-like substance. The secretion as a whole is, at all events, very sticky

**Marloth mentions the use of Roridula as a fly-paper in the manner that Drosophyllum is used in its place of habitation.*

and, bird-lime fashion, captures very many insects, but there is no contributory action of movement in the tentacles (Bruce; Professor Adamson, in a personal letter).

"Commensal" Insects Not Captured

In view of the crowded emplacement of the glands (Bruce, Fenner) and of the great stickiness of the secretion which is abundant on the glands, it is a matter of no small surprise that any insects at all can negotiate the terrain with immunity. How do they do it, is the blunt question which shall now be answered, but perhaps only in part. There are at least five insects which can do so; four above mentioned, and an additional spider observed by Professor R. E. Adamson, according to personal notes received from him recently.

The following observations were made in Munich on the behavior of one of the capsid insects mentioned by Marloth. It came from South Africa along with living plants consigned to the Botanical Institute; evidently Goebel's doing, for his well known interest in carnivorous plants prompted him to gather everything possible from all parts of the world. That some of the insects shared the adventure was a matter of chance, but there they are and they breed and thus replenish their kind from year to year. In August, 1933, there were some half-dozen mature, and twice as many more young, insects. I was thus afforded an opportunity to get some light on the matter of their immunity to the apparent dangers which surround them. This was done chiefly by direct observation, but partly by experiment of sorts.

As regards the contribution of the capsids to the act of pollination, I was able to add little to, or to detract from, Marloth's account. Only a few flowers were available, one at a time. It was observed that only young insects visited the open flowers, and it may very well be that they find sufficiently delicate tissues present to permit them to, and that they do, suck their juices. It is certain, however, that they do not depend upon them for food. I found both old and young insects getting sustenance elsewhere after the flowers had passed. This part of the problem awaits more sustained study where material is sufficiently plentiful.

Aside from this it seems certain that the capsids do not derive any food directly from the plant, and it would indeed surprise us if the spiders (of which three species have been observed by Professor Adamson) are not in the same case. I kept a mature insect (a capsid) in a vial supplied with fresh leaves for several days, during which it probably became anhungered, but I was never able to observe it sucking juices from the leaves. It finally died with food in sight which it had not been able to appropriate. It seems clear that Marloth is quite correct in the view that the relation is commensal—or perhaps we should say mensal, the plant providing a well spread table and the insects being unbidden guests.

But it is a table with menace as well as provision. An unfortunate insect is caught (Plate I—5–7). On a leaf some distance off a capsid spies its flutter-

ings and is not slow to be present for the feast. But in order to come by it, it must pass over many rows of barrier tentacles (Plate I—1–4), which it does swiftly and with no let or hindrance. Not incredulous, for there was the evidence of my own eyes, but most curious, I experimented repeatedly, in a very simple fashion to be sure, by presenting a probe (a needle or fine sedge blade, etc.) to a resting and quiet insect; never was it caught napping, and while yet the menace was far off it would run to hide itself in another position. This repeatedly: up and down both faces of a leaf, around its edges, up the stem and down it (since the leaves are sessile the worst place of all), or out to the farthest tip of a leaf where nothing but tentacles are, and never once hesitating or stumbling from impediment. It is uncanny. Yet there must be an explanation, as there is of the ability of water-skippers to negotiate the water surface. But what is it?

We should note first that it is not because the insect cannot become entangled. I have several times seen my imprisoned specimen, moving slowly in the unusual surrounding of a glass vial, place its foot on a gland and, finding that its claws were sinking in the secretion, withdraw it, pulling out a sticky thread. This it did patiently, lifting the leg higher till the sticky thread broke. The insect then cleaned its foot by rubbing it with other feet till it was clean. Had its foot been supplied with a broad pad (Plate I—9), it is doubtful whether it would have had the strength to pull it away. Since the whole of the capsid's body (and wings) is armed with a covering of fine bristles (Plate I—8), it, like its foot, always presents a minimum surface to the sticky secretion. To test the efficacy of this covering, I endeavored again and again to catch the insect by quickly hitting its back with the glandular edge of a leaf, and was never able to do so. It would be dangerous to say that the immunity of the insect depends solely on this. Possibly many another kind of insect actually captured has a similar armament in which it has no help. There may therefore be something more to the explanation.

That it has long legs from the knees down, raising the body above the tentacles, is probably a factor. The insect can keep its underbody free of the tentacles during movement, though it is not very evident from observation that it never touches its back on them. It occurs to one that there may be some secretion from the insect which repels the glandular resins of the plant but, whether true or not, this is certainly not true of a dead insect.

But again, whatever its equipment for managing the situation, it does require management. The directness and swiftness of the insect's movements have persuaded me that it knows its job. If it does get caught, at least by its foot, it does not blunderingly fall into a panic but carefully behaves with circumspection—or at least it has seemed to me to do so—with the happy result of freedom from capture. Normally, its movements are not slow except while changing its stance while feeding. At other times it usually keeps to the upper or lower surface of the leaf where it is free from glands. When actually feeding, it could often place a foot on a gland unless watchful not

to do so. It may be supposed that the slower its movements the more circumspection could be employed, when it would probably act as my imprisoned specimen did.

Aside from this, the movements are swift and I conceive that this in itself contributes to immunity, for if it treads the glands rapidly its feet do not stick, I believe. Experiment indicates this. Placing a gland under the microscope, it was found that the surface of the gland can be touched with a needle point without its adhering. It was only when some pressure forced the point into the secretion that it adhered. Pulling out a thread of the gum, this usually broke as it did when I observed the insect freeing its caught foot in the vial.

The furniture of the foot with spines and pointed pads (Plate I—9) gives color to the view that the foot can be planted for a brief moment on a gland without danger.

This indicates that the *surface* of the secretion is scarcely at all adhesive. As may be expected, if it is composed of a mixture of resins and caoutchouc (or something akin), and if it contains some water, as it probably does, there will be a surface concentration of less adhesive material which must be broken through before the full effectiveness of the gum is displayed. Thus the insect may be pictured as treading on thin ice, the success of which is in not staying too long in one spot. That this explains also the immunity of the spiders seems equally true, since they, the crab-spiders, are habitually swift of movement. That other insects get readily caught we may suppose is owing less to their size than to the extent of surface for the adherence of the gummy secretion, and their alarm and panic on being caught but a little, leads to consequent floundering to make matters worse.

The spiders, Professor Adamson tells me, live in numbers on every leafy head of the plant. They build among the leaf bases their webby nests, to which they retire in waiting for prey to be caught on the leaves, when they dash out to devour them. The capsids usually rest on the upper or under surface of a leaf, but not exclusively, and soon spotting a caught insect they proceed to suck its juices. When this occurs, the young which are scattered here and there rally around and partake for themselves. Their movements are now quite leisurely. The illustrations show characteristic positions (Plate I—5–7).

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A SINGLE FACTOR MUTATION IN *MELILOTUS ALBA* DESC. HAVING MULTIPLE EFFECTS ON HOMOLOGOUS STRUCTURES[1]

By L. E. Kirk[2] and J. M. Armstrong[3]

Abstract

The multiple effect of a single factor mutation in *Melilotus alba* which affects several diverse characters of the plant including shape of leaflets and petals, position of the staminal column, morphology of the pistil, female fertility and vigor of growth, is described.

The results are significant in showing that one of the genes which presumably determined leaf shape in the species ancestor still continues to modify the shape of those organs which have evolved from the leaf.

It is now generally recognized that factor expression is dependent on the whole genetic complex of an individual and that all factors contribute to a certain end result. On the other hand it is equally clear that in many cases a single factor has multiple effects. In some cases this multiple or pleiotropic effect is apparent in a character, such as pigment development, affecting the whole organism. In other cases the multiple effect is seen on characters which are apparently unrelated. In the present case the effect is apparent on characters which are commonly believed to be phylogenetically related or homologous. Accompanying either of these phenomena due to pleiotropic factors, there may be a disturbance of the physiological or reproductive functions of the organism resulting in decreased vigor of growth and sterility.

An example of several characters being affected by a general pigmentary factor was noted by Mendel in his studies with sweet peas. He observed that plants with purple flowers had red spots in the axils of the leaves and bore brown or gray seeds, while in white flowered plants the red axillary spots were absent and the seeds were white. Tammes (4) records a similar effect of a general pigmentary factor in *Linum usitatissimum* where some of the factors affecting petal color were found to affect anther and seed coat color as well.

Hallquist (1) noted in *Lupinus angustifolius* the pleiotropic effect of a single factor upon unrelated traits where a factor for red flower color increased plant height and induced anthocyanin formation in the stems, and such plants bore seeds with glabrous shiny coats. Morgan *et al* (3) have recorded several cases in *Drosophila* of the manifold effect of a single factor which was frequently accompanied by lowered viability and sterility. One factor which determined rudimentary wings caused a shortening and twisting of the legs as well as female sterility. If crowding occurred or if food conditions were poor the larvae of rudimentary flies died off and in consequence the rudimentary class was smaller than expected.

[1] *Manuscript received May 11, 1934.*
Contribution from the Division of Forage Plants, Central Experimental Farm, Ottawa, Canada.

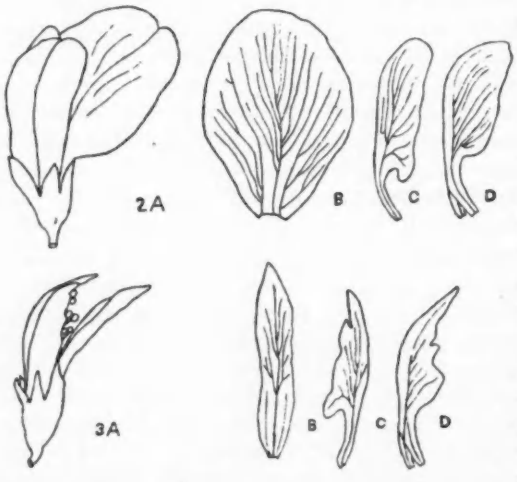
[2] *Dominion Agrostologist.*

[3] *Cytologist.*

A mutation in common white blossomed sweet clover has recently been noted which affords an excellent example of the multiple effect of a single factor on the morphology of the organism accompanied by lowered vigor and sterility. This mutation has been named "Cutleaf" from its most noticeable character effect.

Morphology of the Cutleaf Mutant

The most obvious character affected by the mutant factor is the shape of the leaflets. In normal plants the leaflets are obovate in shape with finely dentate margins. In the mutants the shape of the leaflets is modified to linear while the margins are more coarsely dentate. The petiole of the central leaflet is somewhat bent. These differences are illustrated in Fig. 1. In the course of development the mutant leaves always remain more or less rolled up at the margins, while in the normal plants the leaves are flat and open.



FIGS. 2 and 3. *Camera lucida drawings showing flowers and corolla parts of the normal plant and Cutleaf mutant. 2A, normal flower; 2B, 2C and 2D, standard wing and keel respectively of a normal flower. 3A, Cutleaf flower; 3B, 3C, and 3D, standard, wing and keel respectively of a Cutleaf flower.*

The second character affected is the shape of the corolla parts. Here, as in the case of the leaflets, the petals are much narrower than in normal plants (Figs. 2 and 3). Analogous to the change in leaflet dentation, the keel and wings differ markedly from the normal in having deeply lobed margins.

As a direct consequence of this reduction in the keel and wings the staminal column in mutant flowers emerges from the keel soon after the opening of the flowers (Fig. 3-A). In normal flowers, on the other hand, the release of the tension on the staminal column is brought about by a slight force, usually applied by the proboscis of an insect, and until this force is applied the column remains within the keel.

A fourth difference concerns the pistil. This difference can only be observed microscopically. Fig. 4 shows cross sections through the style and ovary of a normal and a Cutleaf pistil. It is seen that the normal pistil is completely closed, while in the mutant one side has failed to fuse, leaving a longitudinal slit. This slit is located opposite the main vascular bundle or at what may be regarded as the margin of the sporophyll.

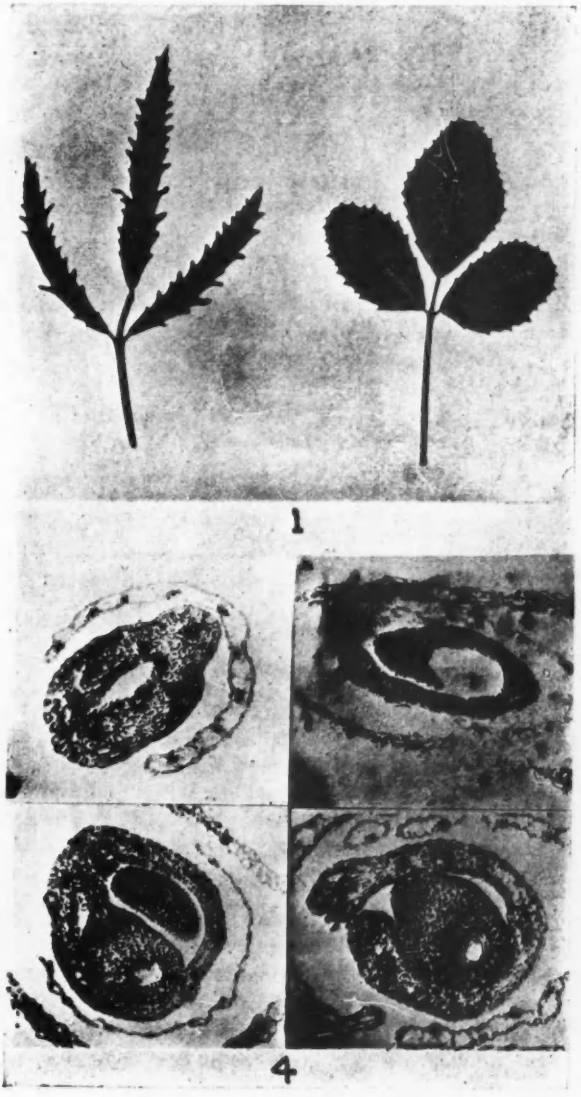


FIG. 1. *Photograph of leaves of Cutleaf and normal plants. Cutleaf to the left and normal to the right.*

FIG. 4. *Photomicrographs of cross sections of the styles and ovaries of normal and Cutleaf pistils. Normal style and ovary to the left and Cutleaf style and ovary to the right.*

The mutant factor thus operates to modify the shape of the leaflets, the petals and the pistil. It also produces accessory effects on the vigor of growth and fertility. The mutant plants when grown in pots of the same size as those used for the normals attain to only about one-half the size. This may be attributed to a decreased rate of metabolism due to the reduced leaf area. The mutant plants flower abundantly but are completely sterile when either their own pollen or that of normal plants is used.

A list of the various characters affected is given in Table I, together with a comparison of normal and mutant plants.

TABLE I

A COMPARISON OF THE CHARACTERS IN NORMAL PLANTS AND IN CUTLEAF MUTANTS

Character	Normal	Cutleaf	Character	Normal	Cutleaf
Leaflet shape	Obovate	Linear	Position of staminal column in newly opened flowers	Within the keel	Outside of the keel
Leaflet margin	Finely dentate	Coarsely dentate			
Petiole of central leaflet	Straight	Bent	Pistil	Entire	Slit longitudinally
Posture of leaflets	Open	Rolled at margins	Vigor of growth	Normal	Greatly reduced
Petal shape	Obovate	Narrow	Fertility	Normal if flowers are manipulated	Completely sterile

Inheritance

Genetic data were obtained by growing progenies of heterozygous plants to the late seedling stage when the two types of segregates could be readily classified. A few plants from each line were then transferred outside in pots in the late autumn of 1933 and exposed to frost for a fortnight to break the biennial resting period. They were then brought back into the greenhouse and cytological and histological studies were made when they reached the flowering stage.

The factor determining morphological changes associated with the Cutleaf character was found to be completely recessive to its normal allelomorph, heterozygous plants being indistinguishable from homozygous normals. As seen from the data presented in Table II, the inheritance is obviously monofactorial. From six out of the seven heterozygous plants tested, normal and Cutleaf progeny appeared in a fairly satisfactory 3 : 1 ratio. Considering each progeny separately the departure from a 3 : 1 expectation is not significant but in all there is a slight but consistent deficiency of the recessive class. This may be due to a lower viability of the seeds in this class since a small percentage of the seeds sown failed to germinate; or it may be due to certation, a decreased rate of pollen tube growth in those microspores of the heterozygous plants which carry the Cutleaf factor.

The ratio obtained in the progeny of Plant 4 differs markedly from that in any of the other families. Among possible explanations may be considered the occurrence of additional new mutations of the Cutleaf factor and trisomic inheritance. The first presupposes a high mutation rate, which is highly improbable; the second was tested by cytological examination of ten normal and two mutant progeny plants, and all showed the normal chromosome number in somatic cells ($2n = 16$). The possibility of Plant 4 being an aneuploid ($2n + 1$) may therefore safely be ruled out. Finally, of course, there is always the chance that a few seeds from a heterozygous plant had become accidently mixed with seeds from a normal plant. But whatever may be the correct explanation, the occurrence of the two recessive mutants in this family of 102 plants does not prejudice the monofactorial hypothesis.

TABLE II

SUMMARY OF F_2 RESULTS ON THE INHERITANCE OF THE CUTLEAF CHARACTER IN SWEET CLOVER

Plant	Normal	Cutleaf	No. of seeds sown
8	150	46	200
9	150	48	200
10	153	45	200
5	33	8	43
7	40	7	50
11	44	13	60
4	102	2	106

Sterility

Kirk and Stevenson (2) showed that *M. alba* is quite variable with respect to self-fertilization. Some individual plants set pods freely both in the field and in the greenhouse, while others, although setting a small proportion of pods in the field produce pods in the greenhouse only after manipulation of the flowers. The normal segregates of the writers' material belong to the second type and fail to produce a single pod in the greenhouse until the flowers are manipulated, in which case pod-setting is fairly good. The Cutleaf mutants proved to be completely self-sterile with or without flower manipulation. An investigation was made to determine whether this was attributable to the male or female organs.

Cytological examination of mature pollen of the normal and Cutleaf plants showed that in both cases it was morphologically very good, the normal giving $94.8 \pm .28\%$, and the Cutleaf $95.4 \pm .55\%$. Germination of the pollen was tested in a culture medium consisting of 12% of sucrose, 1% of agar and 89% of distilled water at a temperature of 27° C. In four hours the pollen of all flowers tested showed germination ranging from 60 to 70%. In another test the Cutleaf flowers were manipulated to insure that the pollen would reach the stigma and another set of flowers was pollinated with normal pollen. In both cases the pollinations were completely unsuccessful. These facts appear to indicate that the sterility is not due to the lack of good viable pollen but rather it must be attributed to the defective pistils which have been previously described.

Discussion

The Cutleaf factor mutation responsible for the alteration of leaflet morphology and for the associated changes in the petals and pistil affords an example analogous to the pleiotropic factors, reported in genetic literature, which control general pigment development. If we presuppose a dominant factor for normal shape of leaves, any mutation of this factor might also affect those plant organs which have evolved from leaves.

In the *Pteridophyta* there are many species in which the leaves not only carry on the normal vegetative functions but are spore-bearing organs as well. The order *Filicales* contains a graded series of genera showing the various steps by which certain leaves are set aside as spore-bearing organs or sporophylls, while others retain only the vegetative function. This differentiation of the frond into vegetative leaves and sporophylls reaches a high point of development in horsetails and club-mosses and is the rule in seed plants.

There are doubtless many factors which determine independently the shape of leaves, petals, stamens and pistil, but it is remarkable that a single factor should markedly influence the morphology of all of them at the same time. The mutation described here, with its manifold effect on the leaves and various derived organs, indicates that in *M. alba* there is at least one factor which in the course of evolution has retained a general control over the shape of those organs which have evolved from the primitive leaf.

Although the unbroken association of modified characters in the mutant which are inherited in a simple monofactorial manner indicates a single gene modification, yet the possibility of aneuploidy or chromosome translocation must not be overlooked. The addition to or subtraction from the genome of a single chromosome has been shown in many plants to be effective in disturbing the genic balance resulting in a departure from the normal expression in many characters. The normal chromosome number ($2n=16$) and regular chromosome behavior at meiosis were invariably found in the several plants of the two segregating classes which were examined cytologically. Hence the cytological evidence substantiates the hypothesis of a single gene change.

The other changes, *i.e.*, lowered vigor of growth and sterility, which characterized the mutant plants may be regarded as accessory effects of the morphological modifications. The genetic data presented in Table II show a slight but consistent deficiency of the recessive class. This may be ascribed to certation or to a slightly lowered viability of the seeds. Considering the reduced vigor of the Cutleaf plants, the latter explanation seems the more probable. The pollen produced on the recessive mutants was shown to be as good, and capable of as high percentage germination, as that produced on normal plants, hence it is probable that they are female sterile owing to defective pistils.

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THE EFFECT OF TEMPERATURE UPON THE PRE-ADULT LARVAE OF THE BULB NEMATODE *ANGUILLULINA DIPSACI* (KÜHN, 1858) GERV. AND v. BEN., 1859, IN RELATION TO TIME AND MOISTURE[1]

By R. J. Hastings[2] and W. Newton[3]

Abstract

In a moist environment, a minimum exposure of 120 min. at 110–113°F. is required to destroy pre-adult larvae of the bulb nematode *Anguillulina dipsaci* (Kühn, 1858) Gerv. and v. Ben., 1859, but progressively shorter exposures are required as the temperature is raised. At 116.5–118.5°F. the lethal exposure is 60 min. and at 118.5–120°F. an exposure of 30 min. is required.

In a dry environment exposures of 150 min. to temperatures as high as 140°F. are not lethal to pre-adults and the heat treatment does not affect their ability to induce the characteristic symptoms of infestation in barley seedlings.

The pre-adults are more resistant to heat than any other stage in the life history of the nematode.

The data suggest that the ineffectiveness of the standard hot water treatment when applied late in the season is due to the fact that the major development of pre-adults takes place after the bulbs are lifted, and also because the masses of dormant pre-adults are often well isolated from the moisture of the bath by the bulb scales and corky basal plates, and are more resistant to heat in a dry, compared with a moist, state. It is recommended that the hot water treatment be employed not later than four weeks after lifting when the lifting is done as soon as the foliage dies down.

A pre-soak is suggested as a possible means of increasing the effectiveness of the standard hot water treatment.

The hot water treatment as developed by Ramsbottom (4) and others (5, 6) for the destruction of the parasitic nematode *Anguillulina dipsaci* in narcissus bulbs has been of inestimable value to the bulb growers, yet the writers' experiments and those of others (2, p. 37) show that the treatment frequently fails to destroy all the nematodes, particularly when the bulbs are treated after a long storage period. To account for the discrepancies between the results of different investigators as to the time required to kill the bulb nematode at 110°F. and for the fact that the nematodes are more resistant in bulbs that have dried out, the writers suggested that certain stages in the life history were more resistant than others, and data were presented which proved that pre-adult larvae were less resistant when moist than when dry (1). No previous investigator has taken into consideration the fact that the nematodes in bulbs are not surrounded by water, hence the lethal time and temperature of treatment for nematodes within bulbs are not likely to be the same as those determined when the nematodes are suspended in water.

Experimental

The nematodes used in these experiments were entirely the pre-adult larvae obtained as "wool" from diseased narcissus bulbs. The wool consists

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of conspicuous masses of tightly coiled nematodes, ranging in size from 860 to 1150 μ, which when placed in water may take three to four hours or longer to revive and become motile. The length of time required by the nematodes to revive appeared to vary directly with the time that they had been in the dormant desiccated condition.

The effect of temperature in relation to time and moisture was determined as follows:—Pieces of the wool consisting of about 1000 nematodes were placed in small vials, 2.5 cm. in length, made from thin glass tubing 4 mm. in diameter. The moist environment was created by introducing a drop of water into the vials. The vials were then plugged with rubber stoppers and dropped into a beaker of water maintained at the desired temperature. Upon removal from the hot water, the contents of the vials were shaken out into syracuse dishes of cold water and kept for 24 hr. before microscopic observations were made. Finally, the water suspensions of heated nematodes were used as inoculum by adding them to sterilized soil in 3-in. pots which were seeded to Barks barley. The presence or absence of the raised white spots on the leaves, the characteristic infestation symptoms in the barley seedlings, served to evaluate the influence of temperature and exposure upon the inoculum. The results are shown in Tables I to IV.

TABLE I

THE PERCENTAGE OF MOTILE NEMATODES AFTER EXPOSING MOIST PRE-ADULT LARVAE TO TEMPERATURES OF 110–120° F. FOR DIFFERENT PERIODS OF TIME

Temp., °F.	Exposures, min.								
	30	45	60	75	90	105	120	135	150
110–113	50	10	10	1	0.5	0.5	0	0	0
113–115	10	1	1	0.5	0.5	0	0	0	0
115–116.5	5	5	5	0.5	0	0	0	0	0
116.5–118.5	0.5	0.5	0	0	0	0	0	0	0
118.5–120	0	0	0	0	0	0	0	0	0

TABLE II

THE AMOUNT OF INFESTATION (%) IN BARLEY SEEDLINGS INDUCED BY PRE-ADULT LARVAE EXPOSED TO HEAT FOR 30 AND 60 MIN. IN A MOIST ENVIRONMENT

Temp., °F.	1st sowing, Oct. 7		2nd sowing, Oct. 28		3rd sowing, Dec. 14	
	Exposure		Exposure		Exposure	
	30 min.	60 min.	30 min.	60 min.	30 min.	60 min.
110–113	0	0	30	10	75	20
113–115	0	0	10	5	60	50
115–116.5	0	0	10	10	45	15
116.5–118.5	0	0	10	0	35	10
118.5–120	0	0	0	0	5	5
Check—Untreated nematodes	0		30		50	

TABLE III

THE PERCENTAGE OF MOTILE NEMATODES AFTER EXPOSING DRY PRE-ADULT LARVAE TO TEMPERATURES OF 110–140° F. FOR DIFFERENT PERIODS OF TIME

Temp., °F.	Exposures, min.						
	30	45	60	90	105	120	150
110–113	100	100	100	50+	50+	50+	50+
113–115	100	100	100	50+	50+	50+	50+
115–116.5	100	100	100	50+	50+	50+	50+
116.5–118.5	100	100	100	50+	50+	50+	50+
118.5–120	100	100	100	50+	50+	50+	50+
129–131	90	90	75	50+	50+	50+	50+
138–140	75	75	75	50+	50+	50+	50+

TABLE IV

THE AMOUNT OF INFESTATION (%) IN BARLEY SEEDLINGS INDUCED BY PRE-ADULT LARVAE EXPOSED TO HEAT FOR 30 AND 60 MIN. IN A DRY ENVIRONMENT

Temp., °F.	1st sowing, Oct. 7		2nd sowing, Oct. 28		3rd sowing, Dec. 14	
	Exposures		Exposures		Exposures	
	30 min.	60 min.	30 min.	60 min.	30 min.	60 min.
113–115	10	15	10	10	75	75
115–116.5	10	0	10	50	50	55
116.5–118.5	0	0	50	60	50	40
118.5–120	10	15	30	60	60	60
129–131	0	0	20	70	65	60
138–140	0	0	10	10	55	20
Check—Untreated nematodes	0		30		50	

The data presented in Table I show that in a moist environment, an exposure of 120 min. is lethal at 110–113°F., and the time required to destroy the pre-adult larvae progressively becomes shorter as the temperature is raised. At 116.5 to 118.5°F. a 60 min. exposure is enough, and at 118.5–120°F., only 30 min. is required.

The data in Table II suggest that the exposures given in Table I are minimum values, for there was a survival of nematodes after an exposure of 60 min. at 118.5 to 120°F., and these survivors were capable of infesting barley seedlings (Fig. 1).

The data in Table II also show that successive sowings of barley are sometimes required before the characteristic symptoms of nematode infestation develop in the barley seedlings. As pointed out in a previous publication (3) barley seedlings develop characteristic symptoms only when the environment favors a stocky growth.

The data in Tables III and IV show that in a dry environment temperatures as high as 140°F. for 60 min. are not lethal to the pre-adult larvae, and that the heat treatment does not prevent them from inducing the characteristic infestation symptoms in barley seedlings (Fig. 2).

The nematode "wool" consists entirely of pre-adults and it will be seen from the data in Table V that this stage is much more resistant to heat than younger stages and slightly more resistant than adults. A mixture of adults, pre-adults, half-grown and very young larvae together with eggs, was teased out of green narcissus leaves and water suspensions were subjected to a temperature of 110–112°F. for 30 and 60 min. These were examined six hours later for motility, and again 96 hr. later for the possible presence of freshly hatched larvae from viable eggs. The percentage motility in each class was based upon a count of not less than 50.

TABLE V

THE EFFECT OF EXPOSING VARIOUS STAGES OF NEMATODES TO A TEMPERATURE OF 110–112° F.

Exposure, min.	Stages and average size				
	Adults, 1300–1400 μ	Pre-adults, 720–1200 μ	Half-grown larvae, 570–720 μ	Very young larvae, 340–570 μ	Eggs
	% Motile				% Viable
30	18	19	0	0	0
60	4	10	0	0	0

Conclusions

These results have an important bearing upon bulb sterilization by immersion in water at 110–112°F. Owing to the greater resistance to heat of pre-adults compared with other stages in the life history of the organism, it is apparent that the treatment should be given as early as possible, for the major development of pre-adults takes place after the bulbs begin to ripen. Furthermore, bulbs frequently lose considerable water in storage, and the writers' results show that dry pre-adults are more resistant than those that have been activated by moisture. The "wool", or masses of pre-adult larvae, begins to form under dry storage conditions shortly after the bulbs are lifted, and masses of dormant pre-adults are often well isolated from the moisture of the bath by the corky basal plate and the bulb scales, although the conspicuous "wool" is usually observed around the exterior of the basal plate. Under the climatic conditions of the coast of British Columbia, these masses of dormant pre-adults have been found after six weeks of storage, hence it is recommended that the bulbs should be passed through the hot water not later than four weeks after lifting, when the lifting is done as soon as the foliage dies down.

1

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FIG. 1. *The amount of infestation in barley seedlings induced by pre-adult larvae exposed to 118.5–120° F. for 30 and 60 min. in a moist environment.*

FIG. 2. *The amount of infestation in barley seedlings induced by pre-adult larvae exposed to 138–140° F. for 30 and 60 min. in a dry environment.*

The writers' conclusion that the hot water treatment should be employed early rather than late is supported by field studies. A Vancouver Island grower treated one lot of King Alfred bulbs in early August and the remainder in October. No infestation was found in those treated in early August, while 30% were found infested in those treated in October.

In view of the marked resistance of the dormant pre-adult larvae of *Anguillulina dipsaci*, particularly when in a dry condition, it is probable that the hot water treatment of other bulbs, plants and seeds in which the nematodes occur internally, may have to be re-investigated. The lowering of the resistance to heat of pre-adult larvae through absorption of water suggests the advantage of a pre-soak before the immersion of bulbs, plants or seeds in hot water.

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A COMPARISON OF THE ROUTINE RAPID WHOLE BLOOD (STAINED ANTIGEN) AND THE ROUTINE RAPID SERUM AGGLUTINATION TESTS FOR PULLORUM DISEASE[1]

By Jacob Biely[2] and W. Roach[3]

Abstract

Data are presented on 4,429 birds, comprising eight flocks, which were tested for pullorum disease by the whole blood agglutination test and the rapid serum agglutination test (commercial laboratory). The diagnoses agreed in the cases of 4,046 birds (97.24%) and disagreed in the cases of 122 birds (2.75%).

Of the 122 birds, 43 were diagnosed as positive by the whole blood agglutination test and as negative by the rapid serum agglutination test, while 79 were diagnosed as positive by the rapid serum agglutination test and as negative by the whole blood agglutination test.

Of the 122 birds, 102 were retested by the whole blood, rapid serum (Laboratory 1), and rapid serum agglutination test (Laboratory 2, (Experiment Station Laboratory)).

There was a closer agreement between the diagnoses made on the basis of the whole blood and rapid serum tests (Laboratory 2) than between those made on the basis of the rapid serum (Laboratory 1) and rapid serum (Laboratory 2) tests (71.56% and 62.37% respectively).

A detailed study of the retests and post-mortem examination of the 102 birds is presented.

In previous papers (2, 3) the writers reported on the comparative accuracy of the whole blood agglutination test (stained antigen), rapid serum and tube agglutination tests for the detection of carriers of pullorum disease. Papers published by other investigators confirm the conclusion of the writers that the whole blood agglutination test, when applied by a trained technician, provides an accurate, rapid and efficient means of diagnosing pullorum disease.

The purpose of the present paper is to report the results obtained from a comparative study of the routine whole blood agglutination test as conducted in the field, with the routine rapid serum agglutination test as conducted by a commercial laboratory.

Material and Methods

The whole blood agglutination test was carried out by four persons—*A*, *B*, *C* and *D*,—the last, *D*, instructing the others in the technique and interpretation of the tests, as the testing proceeded. The methods followed were those already described by Biely and Roach (2). Simultaneously with the drawing of a drop of blood for the whole blood test, blood samples were taken for the rapid serum test. These samples were shipped at once to a commercial laboratory nearby, where they were tested by the usual technique employed in the rapid serum agglutination test.

Data

Data were collected on 4,429 birds, comprising eight S.C.W. Leghorn breeding flocks. In every one of the eight flocks, positive reactors were found,

[1] *Manuscript received March 29, 1934.*

[2] *Investigation conducted privately by the senior author while employed on a special problem in poultry diseases at the University of British Columbia.*

[3] *Fieldman.*

thus providing excellent material for a comparative study of the whole blood and the rapid serum agglutination tests. The results are shown in detail in Table II, and are summarized in Table I.

TABLE I

SUMMARY OF RESULTS

	No.	%
Positive to the whole blood and positive to the rapid serum	261	5.89
Negative to the whole bood and negative to the rapid serum	4046	91.35
Negative to the whole blood and positive to the rapid serum	79	1.78
Positive to the whole blood and negative to the rapid serum	43	.97

Association coefficient according to the method of Yule (4) = 0.994.

TABLE II

COMPARISON OF RAPID WHOLE BLOOD (STAINED ANTIGEN) AND RAPID SERUM AGGLUTINATION TESTS FOR PULLORUM DISEASE

Technician by whole blood test	Group	No. tests	Number of diagnoses in which both tests agreed				Total agreement		Number of diagnoses in which the tests disagreed				Total disagreement	
			Negative		Positive				P—Whole blood N—Rapid serum		P—Rapid serum N—Whole blood			
			No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
A	1	264	255	96.59	6	2.26	261	98.8	2	0.75	1	0.38	3	1.13
	2	320	316	98.75	3	0.93	319	99.6	1	0.31			1	0.31
	3	251	247	98.41	1	0.39	248	98.8	3	1.19			3	1.19
	4	290	284	97.93			284	97.9	1	0.34	5	1.72	6	2.06
	5	284	213	74.99	64	22.57	277	97.5	3	1.05	4	1.41	7	2.46
B	6	167	162	96.96	4	2.25	166	99.4	1	0.59			1	0.59
	7	411	407	99.02	1	0.24	408	99.46	1	0.24	2	0.48	3	0.73
	8	456	414	90.78	22	4.82	436	95.61	3	0.65	17	3.72	20	4.38
	9	48	34	70.87	6	12.50	40	83.3	3	6.25	5	10.41	8	16.66
	10	147	121	82.31	22	14.97	143	97.28	1	0.68	3	2.04	4	2.72
C	11	314	305	97.13	1	0.31	306	97.45	8	2.54			8	2.54
	12	512	496	96.87	12	2.34	508	99.21	1	0.19	3	0.58	4	0.78
	13	288	219	76.04	55	19.09	274	95.13	10	3.46	4	1.38	14	4.86
	14	204	177	86.77	22	10.78	199	97.54	2	0.98	3	1.46	5	2.45
D	15	72	70	97.22	1	1.38	71	98.61			1	1.38	1	1.38
	16	331	263	79.45	36	10.87	299	90.33	3	0.90	29	8.76	32	9.67
	17	70	63	90.00	5	7.14	68	97.14			2	2.85	2	2.85
Totals														
A		1409	1315	93.32	74	5.25	1389	98.58	10	0.70	10	0.70	20	1.41
B		1229	1138	92.68	55	4.48	1193	97.07	9	0.73	27	2.20	36	2.93
C		1318	1197	90.82	90	6.82	1287	97.64	21	1.59	10	0.75	31	2.33
D		473	396	83.72	42	8.88	438	92.6	3	0.63	32	6.76	35	7.39
		4429	4046	91.35	261	5.89	4307	97.24	43	0.97	79	1.78	122	2.75

P—*Positive*; N—*Negative*.

An association coefficient of 0.994 is very high. In only 2.75%* (1.78% + 0.97%) of the diagnoses was there disagreement.

It will be seen from Table II that in 13 of the 17 groups of birds the agreement between the whole blood test and the rapid serum test was over 97%. In the remaining four groups (Nos. 9, 16, 13 and 8) the agreement was 83.3, 90.3, 95.1 and 95.6% respectively.

No particular significance can be attached to the fact that technicians *A*, *B* and *C* obtained an agreement of over 97%, while technician *D* obtained an agreement of 92.6% only. As already stated above, technician *D* supervised the testing of *A*, *B* and C, and the final diagnoses were subject to his confirmation.

Although a total disagreement of 2.75% between the diagnosis of the whole blood and the rapid serum tests is not statistically significant, it seemed important to determine the reasons for these differences. Are they due to errors in technique, errors in diagnosis, low agglutinin titre of birds or sensitivity of the antigens *per se*? In order to obtain some light on these questions, retests of birds on which there was disagreement by the whole blood and the rapid serum agglutination tests were undertaken. For this purpose, the birds were collected from the various farms and centralized in one house. Since 20 of the 122 birds upon which there were disagreements in the diagnoses had either been sold or had had their bands removed, only 102 out of the 122 birds were available for retest purposes.

The birds were renumbered and blood samples taken in duplicate, and sent for *retest* to the previously mentioned commercial laboratory (designated hereafter as Laboratory 1), as well as to a second laboratory (Experiment Station Laboratory, hereafter designated as Laboratory 2). Simultaneously retests by the whole blood agglutination test were made by Technician *D*.

The diagnoses obtained with the 102 blood samples on the first test (whole blood test, and rapid serum test, Laboratory 1), and the second test (whole blood test, rapid serum test, Laboratory 1; rapid serum, Laboratory 2) are set forth in Table III.† In order to facilitate a rapid analysis of the data, the results of the various tests are summarized in tabular form.

The diagnoses of the first and second tests by the whole blood test and the rapid serum test, Laboratory 1, are compared in Table IV.

It will be seen from Table IV that a change of diagnosis (positive to negative or *vice versa*) was recorded in 13 cases by the whole blood test and in 32 cases by the rapid serum test. Since the interval between the first and second tests varied from two to nine days, the changes in diagnoses would not probably be due to marked variations in the agglutinin content of the blood sera of the respective fowls. The changes would more likely be due to faulty diagnosis made in either of the two tests.

**This 2.75% is obtained by dividing the 122 cases of disagreement by the total of 4,429 birds of which 4,046 were totally non-reactive, rather than by 383 the total number of reactors to either test. On this latter basis the percentage disagreement is 31.9%.* (Editor's note.)

†Details may be obtained from the author or the Editor of the Canadian Journal of Research.

The results of the second tests of the 101 birds which were recorded as disagreements with the first test show that the whole blood test and the rapid serum test, Laboratory 1, agreed in 11 positive diagnoses and in 27 negative diagnoses, a total agreement of 38, or 37.6%. There were three birds in which the diagnoses by both tests were inconsistent. In the case of 60 birds there was still a disagreement in diagnosis between the whole blood test and the rapid serum test, Laboratory 1. This is shown in the following summary:—

—	Whole blood agglutination test	Rapid serum agglutination test, Lab. 1
1. Agreed positives on the 2nd test that were diagnosed as negatives on the 1st test	3	8
2. Agreed negatives on the 2nd test that were diagnosed as positives on the 1st test	6	21

3. Inconsistent diagnoses recorded by both tests:—

Bird No.	Whole blood agglutination test		Rapid serum agglutination test—Lab. 1	
	1st test	2nd test	1st test	2nd test
3077	P	N	N	P
3143	SP	N	N	PP
3167	P	N	N	PP

P, PP = Positive; SP = Suspicious positive; N = Negative.

4. Disagreements between the whole blood test and the rapid serum test, Laboratory 1.

Positive to the whole blood test—negative to the rapid serum test,	15
Negative to the whole blood test—positive to the rapid serum test,	45
Total	60

The disagreement between the whole blood and rapid serum tests recorded in Table II is thus reduced from 122 to 81 (including the 21 birds that were not retested). On the basis of 4,429 birds originally tested, the disagreement is 1.82%.

Table V shows a comparison of the diagnoses by the whole blood test and the rapid serum test (Laboratory 2). It will be seen that both on the first and second tests, twelve birds were recorded as negative to the whole blood test that were positive to the rapid serum test, Laboratory 2. These birds are listed in Table VI.

Of these, three were positive to the first and negative to the second whole blood test, while three were negative to the first but positive to the

TABLE IV

COMPARISON OF DIAGNOSES BY FIRST AND SECOND TESTS

Whole blood agglutination test		Rapid serum agglutination test	
Diagnoses unchanged		*Diagnoses unchanged*	
Positive,	22	Positive,	48
Negative,	67	Negative,	21
Total	89 (87.25%)	Total	69 (68.31%)
Diagnoses changed		*Diagnoses changed*	
Positive to negative,	10	Positive to negative,	21
Negative to positive,	3	Negative to positive,	11
Total	13 (12.74%)	Total	32 (31.68%)

NOTE.—*Inadvertently, one blood sample was not sent to Laboratory 1 for retest, hence total number of blood samples is 101.*

TABLE V

COMPARISON OF DIAGNOSES BY WHOLE BLOOD AND RAPID SERUM AGGLUTINATION TESTS, LABORATORY 2

	W.B.	R.S. Lab. 2	No. of birds on which the diagnosis agreed	—	No. of birds on which the diagnosis disagreed
First test					
Positive	33	21	9	Pos. W. B. to neg. R. S.	23
Negative	69	81	58	Neg. W. B. to pos. R. S.	12
Total	102	102	67		35
Per cent			65.68		43.31
Second test					
Positive	26	21	9	Pos. W. B. to neg. R. S.	17
Negative	76	81	64	Neg. W. B. to pos. R. S.	12
Total	102	102	73		29
Per cent			71.56		28.43

NOTE.—W. B. = *whole blood agglutination test.* R. S. = *rapid serum agglutination test.*

TABLE VI

BIRDS WHICH REACTED NEGATIVE TO FIRST AND SECOND WHOLE BLOOD TESTS, BUT WHICH WERE POSITIVE TO RAPID SERUM AGGLUTINATION TEST, LABORATORY 2

1st test	2nd test
Bird number	
3023	
3029	
3207	
3593	3593
3678	3678
3727	3727
3739	3739
3850	3850
3984	3984
4007	4007
4181	4181
4201	4201
	3077
	3143
	3167

second whole blood test. Of the 21 birds that reacted positive to the rapid serum test (Laboratory 2), 9 failed to react to both the first and second whole blood tests. The failure of these nine birds to react positively to the whole blood test cannot be attributed to error in technique, but rather to lack of sensitivity of the antigen or low agglutinin content of the sera. On the other hand, 23 birds (1st test) and 17 (2nd test) were diagnosed positive by the whole blood, but negative by the rapid serum test (Laboratory 2).

The data in Table VII show that the first rapid serum test (Laboratory 1) diagnosed as negative nine birds that were positive to the rapid serum test (Laboratory 2). On the second test, the rapid serum test (Laboratory 1) showed as positive all the birds that were diagnosed as positive by the rapid serum test (Laboratory 2). But, since Laboratory 1 diagnosed a number of birds as positive that were negative to the Laboratory 2 test, the disagreement between the first and second rapid

serum tests (Laboratory 1) and the rapid serum test (Laboratory 2), was 65.34 and 37.62% respectively.

In comparing Tables V and VII it will be seen that the agreement between the diagnoses of the first and second whole blood tests and the rapid serum test (Laboratory 2), was 65.65 and 71.5% respectively, while the agreement between the first and second rapid serum tests (Laboratory 1) and the rapid serum test (Laboratory 2) was 34.65 and 62.3% respectively. There was thus a closer agreement between the whole blood test and the rapid serum test (Laboratory 2) than between the rapid serum test (Laboratory 1) and the rapid serum test (Laboratory 2).

TABLE VII

COMPARISON OF DIAGNOSES BY RAPID SERUM AGGLUTINATION TESTS BY LABORATORY 1 AND LABORATORY 2

	Lab. 1	Lab. 2	No. of birds on which the diagnosis agreed	—	No. of birds on which the diagnosis disagreed
First test					
Positive	69	21	12	Pos. Lab. 1 to Neg. Lab. 2	57
Negative	32	80	23	Neg. Lab. 1 to Pos. Lab. 2	9
Total	101	101	35		66
Per cent			34.65		65.34
Second test					
Positive	59	21	21	Pos. Lab. 1 to Neg. Lab. 2	38
Negative	42	80	42	Neg. Lab. 2 to Pos. Lab. 1	0
Total	101	101	63		38
Per cent			65.34		37.62

Post-mortem Examination

To obtain further information regarding the relative diagnostic value of the whole blood agglutination test and the rapid serum agglutination test as conducted by Laboratory 1 and Laboratory 2, the birds were killed and a careful post-mortem examination was made. Eighty-eight of the birds were examined by the senior author, and 12 birds, by Laboratory 2, while two birds that died from intervening causes were not examined. The results of the post-mortem examination are shown in Table III,* together with the agglutination test diagnoses of the birds that were retested. Since Laboratory 2 conducted additional agglutination tests with the 12 birds, the results of the retests and post-mortem examination are shown separately in Table VIII. The post-mortem examinations were conducted according to the technique described in a previous paper (2).

* *See second footnote p. 800.*

From a consideration of Table III* it was observed that out of 21 birds that were diagnosed as positive by the tube and rapid serum agglutination tests (Laboratory 2), *S. pullorum* was isolated from 13 birds, or 57.1%. *S. pullorum* was not isolated from any of the birds found positive by Laboratory 1, but negative by Laboratory 2. With the exception of two cases, *S. pullorum* was not isolated from any of the birds diagnosed positive by the whole blood agglutination test but negative by Laboratory 2.

The comparatively small percentage of birds from which *S. pullorum* was isolated was due to the fact that out of the 102 birds in which there was a disagreement between the whole blood agglutination test and the rapid serum agglutination test (Laboratory 1), 81 birds were apparently negative (as shown by Laboratory 2), while of the remaining 21 positive birds, several were borderline or doubtful reactors. This is clearly brought out in Table VIII, which shows that not one of the six birds which were diagnosed as positive by Laboratory 2 rapid serum and tube agglutination tests gave a definite reaction in a 1 : 100 dilution by the tube agglutination test. Furthermore, these six birds showed slight fluctuations in reaction from test to test.

TABLE VIII

DETAILS OF RETESTS ON TWELVE BIRDS AUTOPSIED BY LABORATORY 2

Number of bird	Whole blood	Rapid serum—Lab. 1			Rapid serum—Lab. 2	Rapid serum—Lab. 2	Tube 1 : 100 dil.—Lab. 2	Rapid serum—Lab. 2	Rapid serum—Lab. 2	Tube 1 : 100 dil.—Lab. 2	Rapid serum—Lab. 2	Rapid serum—Lab. 2	Tube 1 : 100 dil.—Lab. 2	Diagnosis—Lab. 2	Post-mortem findings	
															Macroscopic	Bacteriological
	1 2	1	2	3	Sept. 30, 1933			Oct. 17, 1933			Oct. 25, 1933					
2910	P P	N	N	—	—			—	—	—	—	—	—	N	No lesions	Negative
2954	P P	N	N	—	—			—	—	—	—	—	—	N	No lesions	Negative
3023	N P	P	P	†††	†††	†††	†††	†††	†††	†††?	†††	†††	††?	P	No lesions	Negative
3207	N N	P	P	††	†††	†††	††	††	††	—?	††?	††	—?	P	Two typical ova; one suspicious	*S. pullorum*
3305	P P	N	N	†	—			††?	††?	—	—	—	—	N	No lesions	Negative
3487	P N	N	N	—	—			—	—	—	—	—	—	N	No lesions	Negative
3510	P N	N	N	—	—			—	—	—	—	—	—	N	No lesions	Negative
3573	P N	N	N	—	††?	†?	—?	—	—	—	—	—	—	N	No lesions	Negative
3727	N P	N	P	††	†††	††	†††?	†††?	†††?	†	††	††	††?	P	Two typical ova; two suspicious	*S. pullorum*
3739	N P	F	P	†††	†††	†††	†††	†††	†††	†††	†††	†††	†††?	P	No lesions	Negative
3850	N N	P	P	†††	†††	†††	†††	†††	†††	††?	†††	†††	††?	P	No lesions	Negative
3984	N N	P	P	††	†††	†††	†††	†††?	††	††	††	††	††	P	Five typical ova	*S. pullorum*

NOTE.—*1—Routine test. 2—Retest. 3—Second retest. P = Positive. N = Negative.*
†††, †† = Positive. †, — = Negative. ? = Doubtful.
**See second footnote on p. 800.*

Discussion

The present study shows that on the basis of the first routine whole blood agglutination test, 12 birds, and on the basis of the first rapid serum agglutination test, 9 birds, that were subsequently shown to be positive by the rapid serum agglutination test (Laboratory 2) were diagnosed as negative birds. The remaining disagreements were due to birds that were diagnosed by the whole blood and rapid serum agglutination tests (Laboratory 1) as positive, but as negative by the rapid serum agglutination test (Laboratory 2). The fact that the whole blood and rapid serum agglutination tests failed to detect a total of 21 positive birds is more important than the fact that 81 birds that were diagnosed as positive by the whole blood and rapid serum (Laboratory 1), were negative according to the test of Laboratory 2. With regard to control or eradication of pullorum disease, the disagreement in the diagnoses of positive birds between the whole blood and rapid serum agglutination tests was 21 out of 4,429 birds, or 0.47%.*

Considerable work has already been done to show that the serum test is an accurate and valuable means of diagnosing pullorum disease carriers. While it is true that the serum test permits a more exact diagnosis of pullorum disease, both the rapid and the tube tests are nevertheless subject to error. In the final analysis, the accuracy of any laboratory test depends upon the person performing it. The main objection to the whole blood agglutination test is the general claim that it is not sufficiently standardized. The studies of the writers and those of other investigators, show that the antigen is very stable and uniform in quality, while the technique is comparatively simple. The only variable is the personal factor in the interpretation of the results of the reaction. It should not be any more difficult to train men to perform the whole blood agglutination test than to perform the serum agglutination tests.

Since this and previous studies show that there is a close agreement in the diagnoses made on the basis of the whole blood and either the tube or rapid serum agglutination tests, the usefulness of the whole blood agglutination test can no longer be questioned. Furthermore, since it is more adaptable to mass application, its value to poultrymen and to the industry as a whole is so much greater. Since it lends itself so admirably to repeated application at short intervals, it is more practical than either of the other tests.

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**This percentage would be much higher in a heavily infected flock. Assuming, for example, that in the case under consideration all the birds reacting to both tests were affected by the disease, the total number of affected birds was 261 plus 21. The whole blood test left in the flocks 12 birds which constituted a hazard to the remainder, which the rapid serum test left 9 birds. Viewed from the point of diagnosis of the positive birds, therefore, the tests disagreed in a total of 21 out of 282, or 7.4% (instead of 0.47% when the negative birds were also included).* (Editor's note.)

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